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CHEMISTRY—GENERAL

PHYSICAL CHEMISTRY OF PYROMETALLURGICAL PROCESSES. PART II. THE INTERACTION OF LIQUIDS WITH GASES AND SOLID PHASES

(Fizicheskaya Khimiya Pirometallurgicheskikh Protsessov. Chast Vtoraya. Vzaimodeistvie Zhudkostei s Gazami)

By
O. A. Esin
P. V. Gel'd

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Book 2

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O. A. ESIN and P. V. GEL'D

PHYSICAL CHEMISTRY OF PYROMETALLURGICAL PROCESSES:

PART II

THE INTERACTION OF LIQUIDS WITH GASES AND SOLID PHASES

(FIZICHESKAYA KHIMIYA PIROMETALLURGICHESKIKH PROTSESSOV:

CHAST VTORAYA

VZAIMODEISTVIE ZHUDKOSTEI S GAZAMI)

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Chapter VI.

INTERACTION OF GASES WITH METAL AND SLAG.

Gases dissolved in metals are known to exert a substantial influence on the properties of the latter. It is only natural, then, that a great number of investigations was dedicated to the study of this influence. Zhukov, Chizhevsky, and Sieverts, who accomplished classical studies on the solubility of nitrogen and hydrogen in steel, are the pioneers in this field. Later, the works by Karnaukhov and Morozov, Turbin, Samarin, Yavoysky, Chuyko, Nossyreva and others provided a broad analysis of the gas saturation of commercial and pure metals and alloys, contributing thereby to the elucidation of a number of very important production problems.

The present chapter reviews only the simplest systems: gas-metal, gas - slag, and metal - slag - gas, both from the standpoint of their equilibrium conditions and in relation (whenever this was possible) to the dissolution rate of gases. As regards the more complex non-equilibrium system gas - slag - metal, a detailed description of this issue will be found in the monographs by Morozov [1] and Yavoysky [2].

I. THERMODYNAMICS OF GAS INTERACTION WITH METAL

We shall first consider the simplest case - the dissolution of pure gas in metal

$$G_{m(gas)} \rightleftarrows G_{m(solution)}$$

Equilibrium conditions here are determined from the equality of the increments of the molar F_g and the partial-molar $\bar{F}_g$ free energies of gas

$$dF_g = d\bar{F}_g. \qquad \text{(VI, 1)}$$

The first increment can be expressed through volatility f_g of gas in the following manner:

$$dF_g = RTd\ln f_g, \qquad \text{(VI, 2)}$$

and the second may be represented as a total differential with respect to pressure P, temperature T, and concentration N_g of gas

$$d\bar{F}_g = \left(\frac{\partial \bar{F}_g}{\partial P}\right)_{T,N_g} dP + \left(\frac{\partial \bar{F}_g}{\partial T}\right)_{P,N_g} dT + \left(\frac{\partial \bar{F}_g}{\partial N_g}\right)_{P,T} dN_g. \qquad \text{(VI, 3)}$$

As is known, the first partial derivative of equation (VI, 3) is equal to the partial-molar volume $\bar{V}_g$, the second - to the entropy $\bar{S}_g$ with a minus sign, while the third is related to the activity of dissolved gas by the ratio:

$$\left(\frac{\partial \bar{F}_g}{\partial N_g}\right)_{P,T} = \frac{RT}{a_g}. \qquad \text{(VI, 4)}$$

The equation (VI, 1) will then assume the aspect of

$$RTd\ln f_g = \bar{V}_g dP - \bar{S}_g dT + \frac{RT}{a_g} dN_g. \qquad \text{(VI, 5)}$$

We shall consider the equilibrium at any given, though fixed, temperature, i.e., at $dT = 0$. Since the solubility of gases in metals ordinarily is small, the behavior of these systems will deviate relatively little from the behavior of the infinitely dilute solutions, in consequence of which one can assume that

$$a_g \cong N_g.$$

Whereupon

$$\ln f_g = \frac{\bar{V}_g P}{RT} + \ln N_g + C, \qquad \text{(VI, 6)}$$

or

$$\ln \frac{f_g}{N_g} = \frac{\bar{V}_g P}{RT} + C. \qquad \text{(VI, 7)}$$

The resulting equation (VI, 7) relates the volatility and concentration of gas to temperature. In conformity with the rule of phases — according to which the system under survey is bivariant (two components and two phases) — this equation reflects the dependence of gas solubility N_g upon temperature and pressure.

In a number of cases the first item in equation (VI, 7) is small in absolute value and can be neglected, while volatility can be replaced by pressure. Then

$$\ln \frac{f_g}{N_g} \cong \ln \frac{P_g}{N_g} = C, \qquad \text{(VI, 8)}$$

or

$$P_g = KN_g. \qquad \text{(VI, 9)}$$

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In other words, the solubility of gas under these conditions is proportional to its pressure (Henry's law).

If the solution of gas is accompanied by a chemical reaction, for example

$$G_m(\text{gas}) \rightleftarrows \frac{m}{n} G_n(\text{solution})$$

then, with arguments similar to those preceding, it is easy to show that, instead of equation (VI, 7), the following expression will be valid

$$\ln \frac{f_g^{\frac{n}{m}}}{N_g} = \frac{\bar{V}_g P_g}{RT} + C. \qquad \text{(VI, 10)}$$

In particular, if the solution of diatomic gases (m = 2) is accompanied by their dissociation (m = 1), i.e., if

$$G_{2(\text{gas})} \rightleftarrows 2G_{(\text{solution})}$$

then

$$\ln \frac{f_g}{N_g} = \frac{\bar{V}_g P}{RT} + C. \qquad \text{(VI, 11)}$$

For small pressures in this particular case, in passing simultaneously to partial pressures, we obtain instead of equation (VI, 9) the following relationship

$$N_g \sim K\sqrt{P_g}. \qquad \text{(VI, 12)}$$

It indicates that the solubility of gas is now proportional not to the first power, but to a fractional power of gas pressure.

The equation (VI, 12), which was experimentally confirmed by a number of authors, is an approximate one, as this was first emphasized by Krichevsky [3]. It is valid for relatively small pressures.

A few investigators [4], [5], however, found a direct proportionality in their experiments between the solubility of hydrogen in iron and $\sqrt{P_{H_2}}$ at pressures up to 200 atm. and temperatures up to 1550°C, i.e., instead of expression (VI, 11), formula (VI, 12) proved to be valid.

Krichevsky attributes this either to the small influence of the item containing $\bar{V}_H$, or to the fact that the error which is connected with its

rejection, is offset by another one - that of the replacement of volatility by pressure. In the similar way he interprets also Perminov's data [6], according to which the rate of hydrogen diffusion through iron at temperatures of 320-550°C and pressures up to 350 atm is proportional to $\sqrt{P_{H_2}}$.

In general practice such simplifications at high pressures are, of course, inadmissible. It is imperative that the difference between f_i and P_i, the presence of the addend containing $\bar{V}_2$, and the variability of $\bar{V}_2$, be all duly taken into account. The latter is usually small and it is being disregarded. Actually, as shown by Krichevsky and Khazanova [7], who investigated the iron - nitrogen system under high pressures, the two first factors are of primary importance. On the other hand, it is well to underline once more that in the region of moderate pressures the relationships (VI, 9), (VI, 12) and those similar to them prove to be fully applicable.

As to the behavior of gases whose molecules are composed of different atoms, this has not yet been sufficiently investigated. There are grounds to believe that here too dissociation takes place during dissolution.

Thus, for instance, the concentration of SO_2 in copper (see fig. 130) for a variety of temperatures proved to be proportional to $\sqrt[3]{P_{SO_2}}$ [8]. This justifies the belief that the dissolution of SO_2 is accompanied by the disintegration of the molecule into three atoms - S and 2O.

It is reasonable to expect that upon the solution of CO in iron there also occurs a dissociation into carbon and oxygen. The strong catalytic activity of iron with respect to reaction $2CO_{gas} = C + CO_2(gas)$, in particular, speaks in favor of this fact.

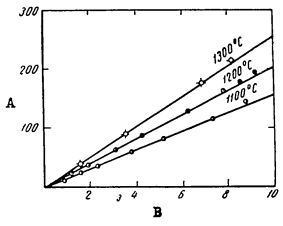

Fig. 130. Effect of pressure and temperature on the solubility S_{SO_2} of sulfurous gas in copper.

Legend: A) Solubility of sulfurous gas S_{SO_2}, $\frac{cm^3}{100g}$.
B) $\sqrt[3]{P_{SO_2}}$, $mm^{1/3}$ Hg.

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Further discussions will deal only with data pertaining to hydrogen, nitrogen, and oxygen.

HYDROGEN AND IRON

According to equation (VI, 12) the dependence of the solubility S_H of hydrogen in metal upon its partial pressure in the gaseous phase conforms to equation

$$S_H = K\sqrt{p_{H_2}}. \qquad \text{(VI, 13)}$$

To what extent this relationship is operative can be seen, for example, from Karnaukhov's and Morozov's work [9]. They experimented with liquid iron at a temperature of 1685 ± 15°C, while changing p_{H_2} within 5.72-31.4 mm. Hg. It appeared thereby that the exponent of p_{H_2} is fairly constant, varying within 0.46 and 0.50. Considering the fact that measurements were made at a high temperature, the constancy of the exponent should be assumed as fully satisfactory.

Analogous results were recently obtained also by other investigators [10]. In these tests total pressure was maintained as constant, while p_{H_2} was being changed through introduction of helium into the gaseous phase.

The parabolic relationship (VI, 13) of hydrogen solubility in iron versus p_{H_2} persisted, as shown by measurements, over broad temperature and pressure ranges. This is illustrated in fig. 131, the curves of which pertain to temperatures varying from 500 to 1550°C and to pressures attaining 130 atm [5].

Let it be noted that the square root law sometimes [11] is being interpreted as a consequence of atomic hydrogen distribution. Indeed, a formal combining of equation (VI, 13) with the expression for the constant D_{H_2} of the dissociation of H_2 in the gaseous phase

$$p_H^2 = D_{H_2} p_{H_2}, \qquad \text{(VI, 14).}$$

leads to the formula of distribution

$$\frac{[\%\ H]}{p_H} = \frac{K}{\sqrt{D_{H_2}}} = L, \qquad \text{(VI, 15)}$$

where [% H] is the equilibrium contents of hydrogen in metal, %.

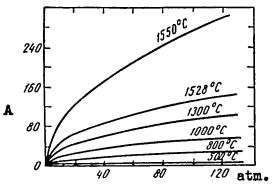

Fig. 131. Effect of pressure and temperature on the solubility of hydrogen in iron.
Legend: A) Solubility of Hydrogen S_H, $\frac{cm^3}{100g}$

However, for moderately elevated temperatures, at which hydrogen is practically undissociated into atoms, p_H is very small and can be hardly attributed the physical significance of pressure. The same can be said about oxygen and nitrogen, the diatomic molecules of which are even more stable.

As to the temperature dependence of hydrogen, for liquid iron Karnaukhov and Morozov [9] suggested the use of the following empirical formula

$$\lg S_H = 0{,}5 \lg p_{H_2} - \frac{1745}{T} + 0{,}888\,. \qquad \text{(VI, 16).}$$

Here S_H - hydrogen contents in iron, cm^3 of H_2 per 100 g. of Fe;

p_{H_2} - partial pressure of hydrogen in the gaseous phase, mm. Hg.

A simple transformation of equation (VI, 16) gives a temperature dependence of the hydrogen solubility constant K in equation (VI, 13)

$$\lg \frac{S_H}{\sqrt{p_{H_2}}} = \lg K = -\frac{1745}{T} + 0{,}888\,. \qquad \text{(VI, 17)}$$

Dyakonov and Samarin [12], on the basis of other authors' data, have selected similar relationships for the different phase states of iron

$$\lg K_{H_2} = -\frac{1250}{T} - 2{,}51\,, \qquad \text{(VI, 18)}$$

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$$\lg K_{H.\,\gamma} = -\frac{1220}{T} - 2{,}335\,, \qquad \text{(VI, 19)}$$

$$\lg K_{H.\,\beta} = -\frac{1340}{T} - 2{,}46\,, \qquad \text{(VI, 20)}$$

$$\lg K_{H.\,\alpha} = -\frac{1530}{T} - 1{,}71\,. \qquad \text{(VI, 21)}$$

A graphic representation of equations (VI, 18) - (VI, 21) is provided in fig. 132. Phase transitions of iron are accompanicd by jumps of lg K, i.e., in the final count, by jumps in solubility of hydrogen.

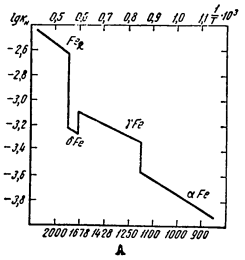

Fig. 132. Isobar of hydrogen solubility in iron.

Legend: A) Temperature, °K

Let it be noted that the data of a number of investigators for solid iron are close enough. For liquid iron, on the contrary, they diverge noticeably. Thus, for example, according to an investigation [13], at the temperature of 1550°C, S_H = 29.2 cm³/100 g., while Karnaukhov and Morozov report S_H = 23.6 cm³/100 g. at 1560°C and S_H = 27.2 cm³/100 g. at 1685°C. This probably is the reason for the divergence of formulas (VI, 17) and (VI, 21).

The same can be said also with regard to the thermal effect ΔH of the solution of hydrogen, which according to the data reported by various authors amounts to, Kcal/g mole H_2:

Karnaukhov and Morozov [9]	.....16 000 ± 1500
Dyakonov and Samarin [12]	.....14 560
Yavoysky [14]	.....17 800
Smitells [15]	.....15 600
Lapp [16]	.....14 500
Liang and others [13]	.....14 550

For solid iron ΔH is somewhat smaller and, according to Armbruster's [17] tabulation, varies within 11300 - 14400 Kcal/g mole H_2.

In conclusion, may it be said that the solubility S_D of deuterium in iron is inferior to that of hydrogen (S_H). In the temperature region of 500-1450°C this difference comprises 0.1-0.9 cm³/100 g. [18]. Yet, when dissolved in palladium $S_D > S_H$, while $\frac{S_H}{S_D}$ varies from 0.67 at a temperature of 300°C up to 0.91 at 1000°C [19].

HYDROGEN AND IRON ALLOYS

Fe - Cr - H System.

Until recently there was no unanimity in the evaluation of the effect of chromium upon the solubility of hydrogen in iron. According to some authors it increases with chromium contents, according to others it drops.

Experiments show that in the solid state iron absorbs hydrogen in greater quantities than chromium [20]. The same data also indicate that with increasing temperature the solubility in chromium grows faster and becomes greater than in iron.

This points to the possibility of a similar relationship of solubility ($S_{H,\,Cr} > S_{H,\,Fe}$) for liquid metals.

Morozov and Gluskin [21] have examined S_H in liquid alloys with low chromium contents (up to 12% Cr). They find that at 1685°C temperature S_H drops with the increase of Cr contents.

On the other hand, the only experiment carried out by them with a rich alloy containing 50% Cr revealed a considerable increase in solubility of hydrogen even if compared with pure iron. This fact again evidences that the relationship $S_{H,\,Cr} > S_{H,\,Fe}$ is possible for liquid metals.

The isotherm plotted by them obeyed the equation (VI, 13). The exponent varied within the narrow limits of 0.47 - 0.52. The solubility thermal effect ΔH for an alloy with 5% Cr proved to be equal to 17500 cal., i.e., differing little from ΔH for pure iron (16000 ± 1500 cal.).

Kurochkin, Yavoysky, and Geld [22] effected measurements of S_H both for poor and rich alloys (up to 90% Cr) at temperatures ranging from 1560 to 1700°C. The results obtained by them are illustrated in fig. 133. In all examined cases solubility grew with temperature. As regards the effect of composition, it proved to be quite complex.

Thus, for example, at a temperature of 1600°C an increase of chromium percentage from 10-12% causes a drop in S_H. Yet, a further increase of chromium contents leads to a rapid growth of S_H. In other words, the

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surveyed isotherm shows a minimum. The foregoing is true for the curves corresponding to temperatures of 1600, 1550, and 500°C. At higher temperatures (1650 and 1700°C) the minimum is absent and addition of chromium leads only to further growth of S_H.

With the lowering of temperature, a broadening of the interval of concentration is to be observed, within the limits of which S_H drops with the growth of chromium contents. This is in perfect agreement with the fact of lower hydrogen solubility in solid chromium than in iron.

Extrapolation of the experimental data permits one to establish S_H for liquid chromium in the conditions of supercooling. At a temperature of 1700°C and a pressure of 760 mm Hg it turned out to be approximately 110 $cm^3/100$ g, whereas at 1650°- it amounted to 80-85 $cm^3/100$ g.

Experiments conducted at three different pressures (277, 495, and 760 mm Hg) confirmed the validity of equation (VI, 13). The value of the exponent varied from 0.47 to 0.60 altogether regardless of the percentage of chromium in the alloy. Moreover, in ten cases out of sixteen the exponent varied within 0.49 to 0.52, i.e., coinciding with the values previously determined by Morozov and Gluskin.

Finally, it should be noted that in case of rapid cooling a considerable proportion of hydrogen evolves from the alloy. As it may be seen from fig. 133, the concentration of the residual hydrogen, while being proportional to its solubility in liquid metal, is still approximately 3 - 3.5 times below it. The considerable evolution of hydrogen during cooling is responsible for the blistered condition of low carbon ferro-chromium [23].

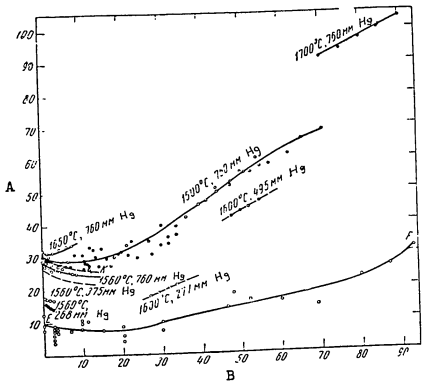

Fig. 133. Hydrogen solubility in ferro-chromium alloys at different temperatures and pressures.

Curve K for 1685°C, 760 mm Hg and curve for 1560°C, 760 mm Hg - according to Morozov's and Gluskin's data. Curve EF - hydrogen concentration in cooled alloy.

Legend: A) Solubility of hydrogen S_H, $\frac{cm^3}{100}$ g

B) Chromium contents, %

Fe - Ni - H and Fe - Co - H Systems

In solid state nickel dissolves hydrogen in a greater proportion than copper, iron, or cobalt (fig. 134). At the melting point there occurs a sharp rise in solubility in each of these metals [15]. The validity of the square root law, i.e., of equation (VI, 13) was experimentally confirmed for nickel over the temperature interval 300-600°C. The expanded relationship with the effect of temperature included [17] assumes the following aspect

$$\lg \eta_{\mu,\,H} = 0{,}5 \lg p_{H_2,\ мм\ Hg} + 1{,}732 - \frac{645}{T}.$$

wherein η_μ is the number of hydrogen micromoles per 100 g of metal.

For liquid Fe-Ni alloys, according to Morozov's and Gluskin's data [21], as well as those of Kurochkin and co-workers [22], hydrogen solubility

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also increases with temperature. As to the effect produced by the composition, the first two authors record a drop in S_H with the increase of nickel percentage (Fig. 135), whereas the second group produced plots with a maximum which corresponds to approximately 4% Ni. All these investigators proved the applicability of expression (VI, 13) to each of the examined alloys. For liquid nickel, as well as for iron, this was also confirmed in other works /10/.

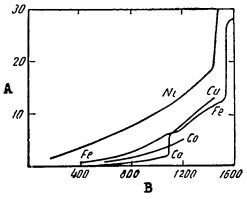

Fig. 134. Effect of temperature upon the solubility of hydrogen in Fe, Ni, Co, and Cu at p_{H_2} = 1 atm.

Legend: A) Solubility of hydrogen S_H, $\frac{cm^3}{100\ g}$

B) Temperature, °C.

In all these investigations the values of the exponent were found to be sufficiently close to 0.5.

The solubility of hydrogen in liquid nickel at 1590°C temperature amounts to 34.2 cm^3/100 g /22/ which is noticeably below Sieverts' data (41.7 cm^3/100 g at 1600°C). The latter, though, seem questionable since they sharply set nickel aside from the closely related analogues.

The heats of H_2 dissolution in Fe-Ni alloys are estimated by Morozov and Gluskin at 15200 cal. at 0.35% Ni, 17000 cal. at 5.65% Ni, and 15500 cal at 10.36% Ni, which corresponds fairly closely to the values for pure liquid iron.

As it may be seen from fig. 134, S_H for solid cobalt is lower than for nickel and iron, but it grows faster with temperature. The effect of small additions of cobalt (up to 4.5%) upon hydrogen solubility in liquid alloys is demonstrated in fig. 136. Like nickel, cobalt in small concentrations also augments S_H.

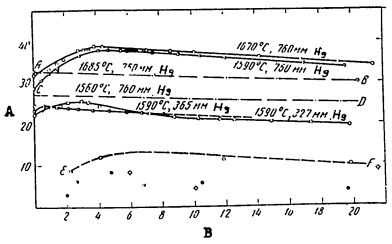

Fig. 135. Hydrogen solubility in Fe and Ni alloys /22/.

Curves AB and CD - according to /21/ data. Curve EF - hydrogen contents in cooled alloy.

Legend: A) Solubility of hydrogen S_H, $\frac{cm^3}{100\ g}$

B) Nickel contents, %

It is possible that a further rise in the percentage of cobalt will lead to a decrease of S_H. The solubility of hydrogen in pure cobalt speaks in favor of such a tendency of the curve. The former proved to be equal /22/ to 37.9 cm^3/100 g at 760 mm. Hg pressure, and a temperature of 1590°C, i.e., somewhat greater (rather than lower) then for liquid nickel (34.2 cm^3/100 g) at the same p_{H_2} and temperature.

The data on hydrogen solubility in liquid Fe-Co alloys at 480 and 735 mm. Hg pressures lead to oscillating p_{H_2} exponent values. They change irregularly within 0.4 and 0.48. The authors /22/ believe that this is caused by errors in measurements and assume that the square root law is applicable also for these alloys.

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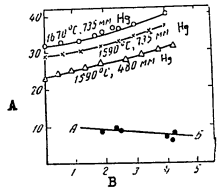

Fig. 136. Effect of cobalt on the solubility of hydrogen in Fe-Co alloys.
Curve A - concentration of hydrogen in cooled alloy.
Legend: A) Solubility of hydrogen S_H, $\frac{cm^3}{100\ g}$
B) Cobalt contents, %

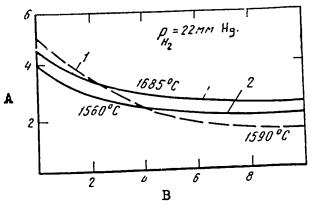

Fig. 137. Hydrogen solubility in Fe-Si alloys: 1 - according to Yavoysky's data; 2 - according to Morozov's data.

Legend: A) Solubility of hydrogen S_H, $\frac{cm^3}{100\ g}$
B) Silicon contents, %

Fe - Si - H System

The isotherm of hydrogen solubility in solid iron-silicon alloys is known to possess a maximum corresponding to approximately 2% Si for gamma iron [24]. Yavoysky was first to study the effect of Si on S_H in liquid Fe-Si alloys [14], [25]. Contrary to the universal belief prevailing at that time, that silicon increases hydrogen solubility in iron, he established the opposite, i.e., that the growth of Si contents actually leads to a decline of S_H. The author attributes this to the formation of silicides which decrease the concentration of free iron.

Later on, Yavoysky's ideas and data were confirmed by other studies [26] as well as by Morozov [17]. His data and the results produced by Yavoysky show an identical character of influence of the Si contents upon S_H (fig. 137).

Fig. 138 represents a family of isotherms of hydrogen solubility in liquid Fe-Si alloys for a broader composition range (from 0 to 65.7% Si) at temperatures of 1400 to 1650°C [26]. All of them have a clearly defined minimum corresponding to the chemical compound FeSi (50 atomic percent). This fact confirms the opinion that the formation of silicides impedes the solution of hydrogen.

It is possible to draw a conclusion on the basis of the plots in fig. 138 that hydrogen solubility in pure liquid silicon is considerable and exceeds somewhat that for iron.

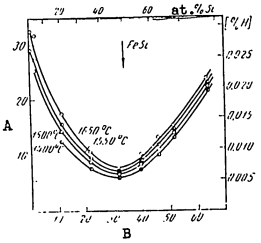

Fig. 138. Influence of the temperature and the composition of Fe-Si alloys on the solubility of hydrogen in them.

Legend: A) Solubility of hydrogen, S_H, $\frac{cm^3}{100\ g}$
B) Silicon contents, %

According to Morozov's data the thermal effect of dissolution grows with the contents of silicon. Thus, for instance,

$$\Delta H_{0.14\%\ Si} = 15\,000\ \text{cal.}, \Delta H_{1.47\%\ Si} = 19\,800\ \text{cal.}$$
$$\text{и } \Delta H_{4.3\%\ Si} = 25\,000\ \text{cal.}$$

Pursuant to the data of other authors [17], [26], which are not as accurate but sufficiently so to permit discussion of the quantitative aspect of the problem, the thermal effect increases initially and then begins to drop with the growth of silicon contents

% Si	0	1,78	11,0	21,7	45,7	51,5	63,7
ΔH	14550	19500	17100	17500	14250	7700	5310

Noteworthy is the fact that a sharp drop of ΔH is observable upon the appearance in the alloy of "free" silicon not combined into FeSi silicide. This also shows that the bond of hydrogen atoms with silicon is more stable than with iron.

Apparently, between free silicon and the atoms of dissolved hydrogen there arise directed bonds responsible for the formation of complexes akin to those of silanes. The possibility of their formation in liquid iron was discussed, for one, by Yavoysky [14].

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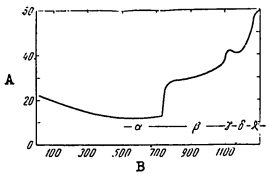

Fig. 139. Effect of temperature upon the solubility of hydrogen in manganese (during heat treatment)

Legend: A) Solubility of hydrogen S_H, $\frac{cm^3}{100\ g}$

B) Temperature, °C

Fe - Mn - H System.

Experiments show that sharply defined jumps in hydrogen solubility (fig. 139) correspond to the phase changes of pure manganese, just as this is the case with iron. These jumps occur [27] at temperatures 727 ($\alpha \longrightarrow \beta$), 1138 ($\gamma \longrightarrow \delta$), and 1245°C ($\delta \longrightarrow$ liquid).

Apart from this, an increase of hydrogen solubility with temperature decline was registered below 500°C [27], [28][1]. The authenticity of this observation, though, calls for additional confirmation. Finally, for the binary Mn-H system the applicability of the square root law as per equation (VI, 13) was established.

According to Yavoysky [14], in liquid iron-manganese alloys a rise in the percentage of the latter component leads to increased hydrogen solubility. The validity of equation (VI, 13) was also confirmed for these alloys. On the basis of the data obtained at temperatures 1548 and 1700°C, Yavoysky was able to determine that the heat of hydrogen solution in the alloys containing 2% Mn, comprises 19700 cal., i.e., somewhat more than in the case of pure iron (17800 cal). For pure manganese it attains 40000 cal/mole according to Morozov's calculations.

Fe - C - H System.

The complexity of the experimental procedure for a long time impeded the study of the influence of carbon upon the solubility of hydrogen in liquid iron. The first data pertaining to this matter were obtained by Karnaukhov and Morozov [9]. They conducted investigations into alloys containing up to 1.5% C over an interval of pressures from 9 to 25 mm, at temperatures ranging from 1530 to 1585°C. The validity was thereby established of the square root law, with the exponent varying within 0.45-0.56, as well as a decline in hydrogen solubility with growing carbon contents.

Similar results were produced later [22]. It was also revealed that the addition up to 7% Cr has practically no effect on S_H in Fe-C-Cr alloys.

Carbon, thus, produces an influence upon hydrogen solubility in iron similar to that of silicon, which apparently should be attributed to the similarity of the status of these elements' atoms in the melt. It is true, though, that silicon reduces S_H somewhat more intensely than carbon in consequence of a greater bond energy with iron.

Other Alloying Elements.

The elements V, Ti, Nb, and Ta are interesting because they are apt to produce comparatively stable complexes containing one or even two atoms of hydrogen. According to the data recorded in Umansky's monograph [29], these complexes may be described by formulas $VH_{0.72}$, $TiH_{1.75}$, $NbH_{0.47}$, and $TaH_{0.78}$.

In spite of the fact that the number of hydrogen atoms varies in them (from 0.47 to 1.75), a number of experiments have revealed that for pure solid vanadium, titanium, niobium, and tantalum, the law of the square root is operative. This circumstance remains unclear and requires further study.

Inasmuch as the formation of hydrides is accompanied by liberation of heat, their stability decreases with growing temperature. It is, probably, on account of this that the considerable solubility of hydrogen in these elements (tens of thousands times greater than in iron) begins to abate with the growth of temperature.

According to Karnaukhov and Morozov [9], the introduction of Ti, Nb, and Ta into liquid iron at temperatures of 1560 and 1685°C leads to a strong rise of S_H. The quantity of heat absorbed during the solution of a mole of oxygen in the alloy decreases sharply thereby. This fact is, no doubt, connected with the exothermic nature of the formation of complexes. The magnitude of the exponent n of p_{H_2} in equation (VI, 13) serves also as an indication of their emergence in the alloy. Even with small additions of the element, it exceeds 0.5 and grows along with the percentage of the addition. For instance, n = 0.55 at 0.45% Ti and n = 0.72 at 3.41% Ti.

The cited authors, on the basis of the inequalities $0.5 < n < 1.0$ found by them, deduce that diatomic hydrides, partially dissociated as per reaction $MeH_2 = Me + 2H$, must be contained in the alloy.

1) This circumstance is analogous to the change of the sign of the temperature coefficient of electrical conductivity as observed during heat treatment of manganese.

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They consider them as groups within the confines of which directed bonds emerge for a definite period of time.

However, for pure tantalum and niobium, no stable hydrides with two hydrogen atoms are known to exist even in the solid state [30]. It, therefore, remains unclear whether it is possible to assume their presence in alloys with iron at high temperatures.

In the conclusion of this paragraph we shall remark that a number of authors [31], [32], [33] have made an attempt, through application of the methods of physical statistics, to write formulas for the solubility of gases in metal. The model of an intrusion solution was put at the basis of the deduction. The particles of gas are arranged along the interstices of the metal lattice; each of them oscillates here until it accumulates sufficient energy to pass into the neighboring interstitial space.

In constituting the distribution function for the system consisting of hydrogen molecules and atoms in the gaseous phase and hydrogen ions in the metal, after a number of approximations, the following expression for solubility is obtained [32]:

$$\lg S_{II} = 2{,}774 + 0{,}5 \lg p - 0{,}25 \lg T - \lg \rho - \frac{\Delta H}{9{,}148\, T}. \qquad \text{(VI, 22)}$$

Here p – pressure, mm Hg;
ρ – density of metal;
ΔH – heat of solution, cal/g mole H_2.

This expression is compared with the experimental data for S_H in iron, nickel, cobalt, copper, and so on.

In the cases dealing with the solubility of hydrogen in hydride-forming metals it is necessary to take into account the localization of the protons, which, in the final count, leads to the equation

$$\lg\left(\frac{S_H}{S_H^{\circ} - S_{II}}\right) = 0{,}242 - 0{,}5 \lg p - 1{,}75 \lg T + \frac{\Delta H}{9{,}148\, T}, \qquad \text{(VI, 23)}$$

in which S_H° relates to the room temperature.

Regrettably both these formulas give only approximate results, with calculated values quite often exceeding 10 times those obtained by experiment.

The works dedicated to the quantum-mechanical analysis of the problem concerning the status of the atoms of a metalloid dissolved in metal are scarce.

Reference should first of all be made to the qualitative interpretation of the effect of hydrogen upon the paramagnetic susceptibility of palladium [31]. It is well known that the latter drops linearly and attains the zero value at 63 atomic percent of hydrogen. In explaining this fact

it is assumed that the hydrogen atoms, when getting into palladium, become ionized and give away their electrons into the d-band. The filling of the latter leads to the compensation of the spin of the unpaired electrons, i.e., to the decrease of paramagnetism. In making use of a model of free electrons, it is possible to demonstrate [34] the validity of the assumption pertaining to the ionization of hydrogen during its dissolution in any metal. However, the semi-classical character of the model, i.e., disregard of the interaction between the electrons in metal, reduces the value of this argument.

Several works [35], [36], [37] are confined to the survey of the electron motion in the periodic field of the lattice distorted by the atom of the admixture. In the presence of a perturbing potential there appear local levels. If they happen to get into the zone of the solvent's conduction, then the electron of the admixture atom (e.g., hydrogen) is being collected. And conversely, if the local level remains between the zones, then the so-called bound state arises and the electrons are retained by the atoms of the impurity. Moreover, under appropriate conditions the metal electrons may pass onto these levels forming a negative ion instead of a neutral admixture atom (for example of oxygen, or sulfur).

However, this reasoning is based on the so-called zonal approximation whereby the interaction of electrons is also disregarded.

In one of the studies [38] a detailed analysis is made of the question dealing with the dissolution of metalloid atoms in metal within the framework of the zonal theory. The work incorporates a wealth of experimental material available both for the postulation of the initial premises and for the evaluation of the results produced.

The energy of the bottom of the conduction band of the solvent metal is composed of three quantities: the energy of sublimation (E_s), the first potential of ionization (E_1) and the Fermi energy of the metal (E_F).

$$E_0 \sim E_s + E_1 + E_F.$$

All of them are negative, since the energy of an electron at rest outside the metal is being taken as the basis of reckoning.

If one compares the absolute values of E_0 and the ionization energy (ϵ) of the atom of the addition, then at $|E_0| > |\epsilon|$ the admixture electron will proceed into the conduction band of the solvent. On the other hand, at $|E_0| < |\epsilon|$ the electron will remain in the admixture.

A calculation made for hydrogen dissolved in copper does not yield an unambiguous answer. Consequently, the energy of the solution of the admixture atoms is being computed. Two alternatives are hereby being considered: 1) the atom is ionized, and 2) the electron remains in a bound state in the atom of the admixture.

The energy of solution is being calculated as a sum of four addends:

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$$E_s = E + E' + E'' + E_2,$$

where E – variation of the energy of Coulomb interaction between the proton and the bound electron as a result of dissolution in the metal lattice;
E' – variation of the energy of Coulomb interaction for conduction electrons (since they are now located in the additional field of the proton and the bound electron);
E'' – the exchange energy between the bound electron and the Fermi electrons of parallel spins;
E_2 – correction for the interaction with the ions of the solvent (copper).

The calculations are being made by quantum-mechanical method. For the case of non-ionized atom the computation produced E_S = – 2.0 electron-volts, and for the ionized E_S' = – 2.85 electron-volts.

In other words the second configuration turned out to be preferable from the point of view of energy, since

$$E_s' < E_s.$$

The experimentally determined heat of hydrogen solution in copper comprised 1.71 electron-volts [32].

Considering the approximation of the calculations, the accord could be regarded as satisfactory.

A similar method was employed for the computation of the heats of solution (in electron-volts) in copper of a few multivalent metals

Metal	Zn	Al	Sn
E_S computed	–0.485	–1.95	–0.53
E_S experimental	–0.355	–1.50	–0.50

Let it be said in conclusion, that a correct solution is possible only as a result of the solution of a many-electron problem with a most complete consideration of all interactions.

SIMULTANEOUS SOLUTION OF HYDROGEN AND OXYGEN IN IRON

An equilibrium establishes itself between the metal and the gaseous phase during the interaction of water vapors with iron (or hydrogen with iron containing oxygen). Definite quantities of oxygen and hydrogen are being thereby simultaneously dissolved in iron. In order to determine a relationship between their concentrations the following procedure was usually practiced [16], [39], [40]. Summing up the following particular reactions

$$2\,Fe + H_{2(gas)} = 2\,FeH,$$
$$Fe + {}^1/_2\,O_{2(gas)} = FeO,$$
$$H_2O_{(gas)} = H_{2(gas)} + {}^1/_2\,O_{2(gas)},$$

a resultative process was obtained

$$3\,Fe + H_2O_{(gas)} \rightleftarrows FeO + 2\,FeH,$$

the equilibrium constant of which

$$K = K_1 \cdot K_2 \cdot K_3 = \frac{[FeO]\,[FeH]^2}{[Fe]^3\,p_{H_2O}} \qquad \text{(VI, 24)}$$

showed that at the given partial water vapor pressure the following interdependence is taking place between the contents of hydrogen and oxygen in metal:

$$[H]^2\,[O] = K' p_{H_2O} = \text{const}. \qquad \text{(VI, 25)}$$

Moreover, temperature dependences were given for K [16] and experimental data confirming the expression (VI, 25) were also recorded for other metals (Ni, Cu). Some authors [42] believed it to be generally impracticable to consider this problem since the solubility of hydrogen in the presence of oxygen is negligible; it is very much lower than in the absence of oxygen from metal.

However, as shown by Morozov and Chuchmarev [43], this question presents an interest from the point of view of principle. In studying hydrogen solubility in liquid iron, they were able to establish experimentally a different relationship than the one recorded above, viz:

$$[H]\,[O] = K'' \sqrt{p_{H_2O}}, \qquad \text{(VI, 26)}$$

where $K''_{1680^\circ C} = 0.064$ and $K''_{1580^\circ C} = 0.022$, if p_{H_2O} is expressed in mm Hg.

To what extent the relationship (VI, 26) is close to reality can be seen from fig. 140 plotted according to the data for $p_{H_2O} = 5$ mm Hg.

Thus, equation (VI, 25) proves to be incorrect. The reason thereof is unclear. It can be attributed either to the inapplicability to this concrete case of the ideal law of mass action, or to the appearance in the metal of some other groups, for example, of hydrogen or oxygen atoms.

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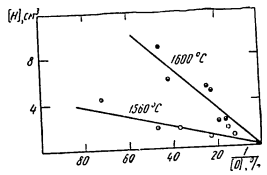

Fig. 140. Relationship between [8] and [10] for iron.

NITROGEN AND IRON

The issues pertaining to the solubility of nitrogen in iron, as well as the peculiarities of the constitution diagram of the Fe-N system (P,T diagram) were made the subject of repeated discussions in literature. Initially a detailed study of iron nitrides (Fe_2N and Fe_4N) was made by Chizhevsky [44]. Krichevsky and Khazanova [7] provided a critical analysis of the works of a number of authors dealing with the calculation of equilibrium in the Fe-N system.

They pointed out the essential errors committed by various investigators (see for example [45]). In the first place there must be the inadmissibility of application of the law of ideal gases. In the equilibria under consideration the pressures of nitrogen attained hundreds of thousands of atmospheres as a result of which volatility differed considerably from pressure. Apart from that, the effect of pressure on the activity of substances in condensed phases was totally disregarded. Finally, no account was taken of the displacement of the boundary lines in the diagram with the growth of pressure.

In view of this they made a new calculation and produced an alternative P,T diagram. They supported it by experiments, carried out over a temperature interval 350-525°C at pressures ranging from 750 to 3800 atm.

Kontorovich and Sovalova [46] as a result of a detailed study of two well known versions of the Fe-N diagram (eutectic and peritectic) arrived at the conclusion that the eutectic diagram is more reliable. Their considerations were later corroborated by experiments [47] with very pure samples of iron. The phase equilibria were studied both through plotting of corresponding interaction isotherms

$$NH_{3(gas)} = N_{(Fe)} + \frac{3}{2} H_{2(gas)},$$

and by X-ray diffraction analysis of the condensed substances.

A more precisely plotted diagram of the eutectic type is recorded in

fig. 141.

The data of a number of authors [48], [49], [50] dealing with the pressure of nitrogen close to atmospheric, were processed by Dyakonov and Samarin [12]. They advanced the following empirical formulas for the temperature dependence of the equilibrium constant of nitrogen solubility in iron:

$$\lg K_{N,\alpha} = -\frac{3660}{T} + 0{,}42, \qquad \text{(VI, 27)}$$

$$\lg K_{N,\gamma} = \frac{371}{T} - 1{,}907, \qquad \text{(VI, 28)}$$

$$\lg K_{N,\varepsilon} = -\frac{2770}{T} + 0{,}35, \qquad \text{(VI, 29)}$$

$$\lg K_{N,\xi} = -\frac{634}{T} - 1{,}06. \qquad \text{(VI, 30)}$$

Dyakonov and Samarin admit the possibility that nitrogen forms nitrides in gamma iron, while in all other phases of iron it remains in the atomic state.

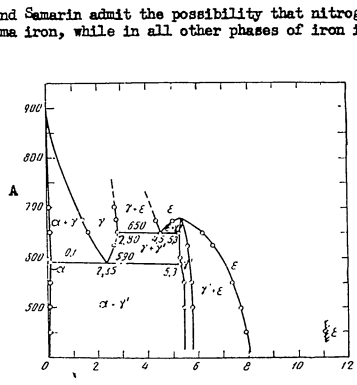

Fig. 141. Phase diagram of the Fe - N system.

Legend: A) Temperature, °C.

The basis for this assumption is constituted by the fact of heat liberation during N_2 solution in gamma iron (ΔH_γ = - 1700 cal/g.atom), and by conformity to the law of the square root. Indeed, the exothermic nature of the process, undoubtedly, points to particularly strong interaction of the N and Fe atoms in the gamma-lattice.

Moreover, it turned out that such thermodynamic characteristics of the N_2 solution process in gamma iron as ΔF_{298} and ΔH_{298} practically

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coincide in magnitude with those of the formation of the Fe_4N nitride.

In view of the fact, however, that nitrogen in intrusion phases, probably, remains in ionized, or more precisely metalline, state, there can hardly arise any co-valent links here between the atoms of nitrogen and iron.

The solubility of nitrogen in liquid iron was lately studied in detail by Karnaukhov and Morozov [51], who, in particular, were able to show that in this case the law of the square root is also applicable. The S_N values obtained by them (for example 0.052% at 1550°C temperature) are somewhat higher than the data of other authors (0.044% at 1550°C [49] and and 0.039% at 1530°C [50]) who used less perfect methods of experimentation.

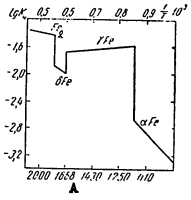

Fig. 142. Isobar of nitrogen solubility in iron (P_{N_2} = 1 atm).

Legend: A) Temperature, °K

In addition to this, they have also established that the thermal effect of dissolution ΔH amounts to 3400 cal/g mole N_2, which differs appreciably from the value ($\sim$ 5800 cal/g mole N_2) used by Dyakonov and Samarin for the development of the above-cited formulas (VI, 27)-(VI, 30).

According to Karnaukhov's and Morozov's figures, the temperature coefficient of nitrogen solubility is very small (fig. 142). It comprises $1.25 \cdot 10^{-5}$% per 1° at 760 mm Hg, which is but little less than the previously found ($1.5 \cdot 10^{-5}$% [50]).

NITROGEN AND IRON ALLOYS

Fe - Cr - N System.

Metallic chromium interacts with nitrogen more energetically than iron. It forms two well known nitrides CrN and Cr_2N the stability of which declines noticeably with growing temperature [52]. It is also known that the rate of nitration of chromium and other metals by ammonia is greater than by nitrogen [53].

The solubility of nitrogen in liquid alloys Fe-Cr naturally increases with the rise in chromium percentage. Morozov and Gluskin [21] have confirmed this experimentally for the alloys which contain up to 10% Cr. In the region of higher chromium concentrations (> 10%) the following relationship is fairly well conformed to [54]:

$$\lg S_N = a + b \lg [Cr], \qquad \text{(VI, 31)}$$

Samarin and Korolev [53] were the first to register this fact.

On the other hand, for poorer alloys (< 10% Cr) the relationship (VI, 31) is not being observed as it may be gathered from fig. 143. Furthermore, here, as over the entire examined range of compositions, solubility fails to obey the rule of mixing, in consequence of which

$$S_{N,\,Fe,\,Cr} \neq S_{N,\,Fe}[Fe] + S_{N,\,Cr}[Cr]. \qquad \text{(VI, 32)}$$

The investigation of the effect of pressure upon nitrogen solubility in liquid Fe-Cr alloys proved the validity of the exponential equation

$$S_N = K p_{N_2}^n, \qquad \text{(VI, 33)}$$

in which n grows together with the contents of chromium.

Moreover, according to Morozov and Gluskin [21], it amounts to 0.9 - 0.95 already at 10% Cr, whilst conforming to other data [54] these values are being reached only at 40-50% Cr.

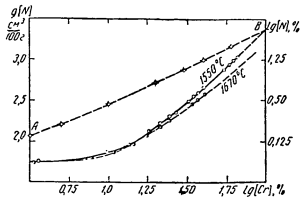

Fig. 143. Influence of chromium concentration upon the solubility of nitrogen in Fe-Cr alloys.

Curve AB was plotted on the basis of the rule of additivity.

The postulate pertaining to the emergence in the alloy of a nitride containing two nitrogen atoms, i.e., CrN_2 [21] encounters with difficulties referred to in the course of the discussion of the Fe-Ta-H and Fe-Nb-H systems. The fact of the matter is that the possibility of the existence of the CrN_2 compound, as emphasized by Proxvirnin [55], has never been

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experimentally proved. In other words, no phase of this composition has ever been produced.

On the other hand, Mozgovoy and Samarin [56] on the basis of X-ray diffraction studies of solid alloys admit the possibility of the formation of Cr_2N nitride. This question still remains unclear and calls for further elaboration. All investigators acknowledge the drop of nitrogen solubility with the rise of temperature and associate this with a partial decomposition of nitrides.

Fe - Si - N and Cr - Si - N Systems.

Silicon produces with nitrogen a number of sufficiently stable nitrides which were thoroughly investigated and synthetized by Chizhevsky [44]. He, in particular, established that these nitrides lose their stability in the presence of liquid iron, i.e., they are easily decomposed by it[1].

The data produced by a number of authors [51], [58] on the solubility of nitrogen in liquid Fe - Si alloys are recorded in fig. 144. The solubility isotherms show a maximum when the concentration of Si is small. As to the initial ascent of the curves, its causes are not sufficiently clear (see, however [51]). The drooping branch, which composes the principal part of the isotherm, on the contrary, is caused by the formation of stable bonds between Fe and Si, i.e., by the decrease of the number of "free" iron atoms, capable of retaining nitrogen in the melt. Actually, the curves intersect the X-axis ($S_N \cong 0$) near the composition corresponding to the FeSi compound.

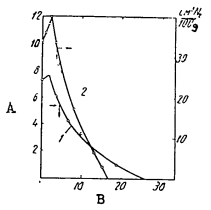

Fig. 144. Solubility of nitrogen in Fe-Si alloys according to the data of:
1 - Karnaukhov and Morozov; 2 - Chipman and Vaughan.

Legend: A) Solubility of nitrogen, $\frac{cm^3}{100\ g}$
B) Silicon contents, %

It should be noted that the drop of nitrogen contents in electric steel with the growth of silicon concentration long ago began to attract the attention of investigators [59], [60].

The studies of Karnaukhov and Morozov [51] disclosed that the solubility of N_2 in Fe-Si alloys changes with pressure in accordance with the square root law. Over the interval of compositions ranging from 1.07 to 12.9% Si the exponent n in equation (VI, 33) varied within the limits of 0.49 - 0.52. This lead the authors to the conclusion that "nitrogen forms with iron and silicon chemical compounds of the Fe_xN and Si_yN types which are dissociated into atoms in a greater or lesser measure".

The study of a related Cr-Si-N system was the basis of the work of Morozov and Samarin [56]. They found that, just as in the case of hydrogen solubility in Fe-Cr alloys, equation (VI, 31) proves to be valid in this instance, i.e., there is a linear relationship between lg S_N and lg [Cr]. It must, however, be noted that, as in the system Fe-Si-N, the rise in silicon concentration leads here to a decrease in nitrogen content.

The solubility of nitrogen, therefore, also is determined by "free" chromium unbound into stable silicides, for example CrSi and Cr_3Si [61].

In view of the above it is hardly possible to expect a strict conformity to expression (VI, 31), since the relation between lg S_N and lg [Cr] loses in this case its linear character. Finally, according to Mozgovoy and Samarin, the temperature dependence

$$\lg S_N = \frac{10\,980}{4.575\,T} + B \qquad \text{(VI, 34)}$$

comprises the same thermal effect ($\Delta H = 10980$ cal) independently from the composition of the alloy. On the other hand, the quantity B is a function of the silicon percentage. This circumstance is similar to the one established for the Fe-Cr-N system [62].

In both cases it is apparently caused by the fact that S_N is determined primarily by the presence of chromium. However, in Fe-Cr alloys the entire amount of chromium is, it seems, participating in the absorption of nitrogen. In the Cr-Si-N system, nitrogen, on the contrary, engages in intensive interaction only with such Cr atoms whose bonds are not satisfied by silicon.

Somehow or other, the thermal effect of solution, calculated per one gram-atom of nitrogen, will be determined mainly by the bonds of Cr with N, i.e., depending little on the presence of the second component in the alloy. Moreover, the magnitude of ΔH must be close to its value for the Cr - N system. Yet, according to Mozgovoy's and Samarin's determination, it appears to be approximately 1.5 times smaller and amounts to only 7600 cal.

1) For the thermal characteristics of Si_2N_4 see [57].

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2. KINETICS OF GAS SOLUTION IN METAL

The process of gas dissolution in metal may be broken down into three successively developing stages:

1) movement of the substance from the nucleus of the gas stream to the interface;
2) adsorption of the molecules, which is usually accompanied by their dissociation, and the event of dissolution proper which is closely connected with it;
3) movement of the dissolved particles into the mass of metal.

Let us first consider experimentally the most thoroughly studied case, when the main inhibitive factor in the kinetics of gas absorption is constituted by the thin surface layer of metal, within the limits of which there develops a two-way diffusion of the gas and metal atoms. In other words, let us suppose that the third stage is the limiting one.

Let us further assume that the gase phase is uni-component, and that the process becomes stationary when its rate u is equal to

$$u = \frac{dg}{dt} = k'S(N_p^\circ - N)\,. \qquad \text{(VI, 35)}$$

Here g - quantity of dissolved substance;
N_p° and N - its solubility at pressure p and concentration in metal;
S - interface area;
k'- coefficient of mass transfer, accounting for convection and diffusion.

Further, if V is the volume of metal, then

$$\begin{aligned} dg &= V dN, \\ \frac{dN}{dt} &= \frac{k'S}{V}(N_p^\circ - N) = k(N_p^\circ - N)\,. \end{aligned} \qquad \text{(VI, 36)}$$

For the given pressure and temperature, N_p° also remains constant.

Hence

$$-\ln(N_p^\circ - N) = kt + \text{const}\,. \qquad \text{(VI, 37)}$$

If, at the same time, at the initial moment (t = 0) the metal was pure (N = 0), then

$$\ln\frac{N_p^\circ}{N_p^\circ - N} = kt\,. \qquad \text{(VI, 38)}$$

As to the deduction of a relationship for the other boundary conditions and for the mixture of gases, it can be found, for example, in the monograph by Ramm [63].

We shall now revert to the constant k. It depends both on the ratio S:V, the surface of metal to its volume, and on k', i.e., on the properties of the dissolving substance and the boundary film. These comprise, for instance, the coefficient of diffusion, viscosity, the surface characteristics of the film, the size of the vessel, the rate and character of mixing. Of great importance for the latter during melting in an induction furnace is the current in the primary circuit, the magnetic properties of metal, and the mutual location of both "windings".

The influence of surface tension σ presents particular interest.

Experiments on the absorption of a number of gases (H_2, N_2, CO, CO_2, Ar, etc.) by water and other liquids, conducted at room temperature, show [64] that σ produces an effect upon the event of dissolution proper only in the case of weakly interacting particles (e.g., Ar and H_2O). Far greater is the significance of σ for the hydrodynamic properties of the film, and consequently, also for the coefficient k.

As demonstrated by Kapitza [65] the wave character of the flow of liquid, even with small Reynolds' numbers (Re = 20 - 25), is more stable than the laminar; with the wave-length proving to be proportional to $\sigma^{0.5}$. According to Frumkin and Levich [66], [67] the capillary active substances, which reduce the surface tension, produce a damping effect on the movement of the surface and thereby considerably decrease the rate of interphase interaction (dissolution, evaporation, and so on).

This was borne out, for instance, by the tests conducted by Sklyarenko, Baranaev, and Mezhuyeva [68], [69], who were able to establish that the rate of vaporization depends on the presence of the adsorption film only in the case if the evaporating substance reduces surface tension. Further, Ternovskaya and Byelopol'sky [70] demonstrated that small additions of surface-active substances (up to 0.01%) produce a considerable effect on the SO_2 dissolution rate in water. Moreover the subsequent increase of their concentration ordinarily affects the kinetics hardly at all.

Finally, Kryukova [71], while investigating the behavior of the venous mercury electrode (the hydrodynamics of which is in many respects similar to the movement of metal in induction furnace), revealed a slowing down of the surface movement under the influence of capillary active substances. For the additions of strong adsorbates the effect may be observed even at very small concentrations (10^{-8}m).

Experimental material dealing with the kinetics of gas absorption by molten metals is very scarce. Most interesting in this respect are the data pertaining to the rates of hydrogen and nitrogen solution by liquid iron obtained by Karnaukhov and Morozov [7], [9], [51]. They heated the metal in an induction furnace, while judging the intensity of the process according to the rate of pressure drop in a closed vessel.

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In view of this equation (VI, 36) was modified in the following manner. First of all

$$N = b(P_{beg.} - P), \qquad \text{(VI, 39)}$$

where $P_{(beg)}$ and P are the pressures at the beginning of the test and at the instant of time t;
b - is the factor of proportionality.

Further, according to the square root law

$$N_p = \delta \sqrt{P}. \qquad \text{(VI, 40)}$$

Then

$$-b\frac{dP}{dt} = k[\delta\sqrt{P} - b(P_{beg.} - P)]. \qquad \text{(VI, 41)}$$

The latter expression may be developed to assume the aspect

$$\frac{df(P)}{dt} = -\frac{d\left[-\lg(m^2 - a^2) + \frac{B}{2a}\lg\frac{m-a}{m+a}\right]}{dt} = -\frac{k}{2{,}303}. \qquad \text{(VI, 42)}$$

Here

$$B = \frac{P_{beg.} - P}{\sqrt{P_{beg.}}}; \quad m = \sqrt{P} + \frac{B}{2}; \quad a = \sqrt{P_{beg.} + \left(\frac{B}{2}\right)^2};$$

P_{pend} is the final pressure in the conditions of equilibrium.

The validity of the diffusion equation (VI, 36) was proved by the authors through the fact that the linear relationship (VI, 42) of f (P) versus time was experimentally corroborated. As to the direct check of the applicability of expression (VI, 37), it was effected for nitrogen by other authors [57], who determined the existence of a direct proportionality between $\ln(N_p^o - N)$ and t at certain temperatures (1540, 1600, 1680, and 1760°C).

The basic results obtained by Karnaukhov and Morozov can be reduced to the following:

The coefficient of mass transfer k related to unit volume does not depend on pressure. For instance, for hydrogen at the temperature of

1685°C and the pressure varying from 9.72 to 412 mm Hg it fluctuated irregularly from 3.0 to 3.4.

The value of k changes with the intensity of current I in the inductor and is in direct proportion to the square of the current intensity, i.e.,

$$k = k_1 I^2.$$

This they attribute to increasing mixing of metal the intensity of which also grows with I^2.

It should be noted that a number of authors [50], [72], [73] did not register any noticeable effect of the temperature upon the coefficient of mass transfer. In this they perceived a confirmation of the diffusion character of the process, overlooking the fact that the rise of temperature in induction furnaces is achieved by means of increasing current intensity I. This in turn leads to intensified mixing which, considering the diffusion character of the process, unavoidably results in its acceleration.

Karnaukhov and Morozov have found that the growth of the volume of metal V, with a constant interface area S, decreases k approximately so as it follows from the ratio $k = k' \frac{S}{V}$ in the expression (VI, 36).

The recorded facts evidence without a shade of doubt that the movement of the substance from the surface of the metal into its bulk constitutes the limiting stage of the process.

By experiments of the same authors it was established that the rate (more precisely k) of hydrogen dissolution is 8-10 times greater than that of nitrogen. This fact can apparently be explained by the relationship of the coefficients of hydrogen and nitrogen diffusion in iron, i.e., by the fact that $D_H > D_N$.

Indeed, under the influence of the electromagnetic field there occurs a movement of metal in the crucible of the induction furnace. Fresh portions of metal move along the axis of the crucible (fig. 145) towards the interface renovating thereby the surface layer. On getting into contact with gas, the metal becomes saturated with it as it moves towards the crucible walls whereupon it mixes up with the general mass.

With the temperature constant and the mixing intensive, the principal kinetic barrier is constituted of the thin film of metal in which only diffusion is taking place. It is precisely this circumstance that permits one to think that the difference in the dissolution rates of H_2 and N_2 is caused by the difference of the diffusion coefficients.

According to Karnaukhov and Morosov, the introduction into iron of alloying additions (Al, Ti, Nb, Cr, Ni) hardly affects the kinetics of solution. Only silicon presents an exception, its additions in proportions of around 1% approximately double the values of k_H and k_N. According to the data of other authors [50], [58] the effect of silicon is considerably

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stronger - k_N grows 20 times upon admixture of 0.7% Si. An appreciable disparity exists also with regard of aluminum - according to the same experiments [50] after addition of 0.15% Al the value of k_N was reported to have increased 12 times.

As was stated earlier, the effect of admixtures on the kinetics of solution may be caused by a variety of reasons. They can affect viscosity, surface tension, and specific resistance of metal, as well as the mode of the existence in it of the dissolved gas.

Where silicon additions are concerned the effectiveness of the introduction of small doses ($\sim$ 1% Si) is noteworthy. In this connection it is well to mention that the solubility of nitrogen (but not of hydrogen) also increases at such concentrations of Si. Possibly, the increase of S_N constitutes one of the reasons for the growth of k_N upon addition of Si. This, however, cannot explain the increase of k_H.

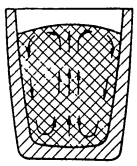

Fig. 145. Diagram of the movement of metal in the crucible of an inductive furnace.

Somewhat surprising is the constancy of k (k_H = 2.9 - 3.0; k_N = 0.79) during further increase of silicon contents (> 1%). As a matter of fact, silicon is surface-active [74] with respect to iron, besides, it augments the resistivity of metal. Both these circumstances should retard dissolving: the first - because of the decreasing turbulence of the surface layer movement, the second - because of the drop in I^2, i.e., of the intensity of mixing[1]). Therefore, the independence of k from the subsequent increase of silicon up to 10%, or nickel up to 20%, or chromium up to 50%, requires elucidation.

It should be noted in conclusion that the kinetics of gas dissolution in metal, apparently, is not determined by diffusion processes in all cases. Let it be remembered that the rate of nitrogen solution in iron and its alloys (e.g., Fe-Cr) is many times greater when NH_3, and not N_2, is present in gas.

If one considers that this is caused by the difference in the energies required to disrupt the bonds in NH_3 and in N_2, than the event of chemical adsorption of gas should be recognized as constituting the retarding stage.

Probably, in connection with analogous circumstances the rate of steel saturation with gases in arc furnaces is greater than in reverberatory units. Indeed, the arc causes a partial dissociation of N_2, H_2, H_2O. The presence of atoms substantially facilitates and accelerates the process of solution.

Chuyko [59], [75], Shatalin [76], and Ageyev [77] were among the first to register this fact. Moreover, for the calculation of nitrogen and hydrogen solubility Chuyko suggested the use of the square root law which also takes due account of the partial dissociation of gas

$$S_N = K_N\sqrt{p^{1+\alpha_N}}\ ;\quad S_H = K_H\sqrt{p^{1+\alpha_H}}\ . \qquad \text{(VI, 43)}$$

In this connection the works [15] and [78] dealing with the saturation of metal with hydrogen are also interesting. It turns out that the rate of this process is appreciably greater than in the case of normal dissolution of hydrogen. The reason here is, apparently, the same as referred to above, namely the presence of the atoms of H along with the molecules of H_2.

3. GASES IN SLAG

The interaction of gases with slags is still far too insufficiently studied. A more or less systematized material is available only for hydrogen, water vapors and partially for nitrogen. This material will be described below.

SOLUBILITY OF GASES IN SILICATES.

Glasses.

A comparatively voluminous experimental material pertaining to the degree and the avenues of saturation of silicates with gases was accumulated as a result of studies of optical and other special glasses. It permits making the assertion that steam and other gases possess a certain degree of solubility in glasses.

Furthermore, with increasing temperature and pressure the solubility of H_2O grows rapidly, and in a number of cases when the contents of H_2O rises up to 20% and more, solid brittle glasses change into thick pastes, the viscosity of which drops with further growth of H_2O contents. Thus the change from solid glasses to common soluble (aqueous) glass may, it seems, be achieved continuously, which fact points to the close affinity

1) It should be borne in mind that at a constant temperature (for example 1685°C) the magnitude of $W \cong I^2R$ is constant, in consequence of which the growth of R leads to a drop of I.

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of the vitreous and liquid states.

In the course of a number of old experiments /79/ confined to the study of gas contents in sodium-lime glasses by means of vacuum extraction, the following was revealed.

The volume of the dissolved gases attains four times the volume of glass. The basic components of gas are: H_2, H_2O, CO_2, SO_2, O_2, and N_2.

A preliminarily outgassed glass dissolves H_2O, but is, allegedly, incapable of absorbing CO_2, O_2 and N_2.

On the basis of this assumption, a conclusion was made to the effect that, with the exception of water vapors, all other gases are "physically" insoluble in glasses and evolve from them only as a result of irreversible decomposition of chemical compounds. However, subsequent investigations have exposed the fallacy of this assumption.

Krassikov /80/ found, in particular, that the blowing of moist CO_2 through liquid glass increases the degree of gas saturation of the latter up to the level characteristic for industrial samples. For instance, in the glass (70% SiO_2, 11% CaO, 11% Na_2O, 4% K_2O) melted in a 140 l-capacity pot, the concentration of gas amounted to around 16 $cm^3/100$ g; the composition of gas being 75% H_2O, 7% CO, 6% H_2, 5% CO_2, 5% O_2, and 0.3% N_2. In laboratory melting the contents of gas before blowing with moist CO_2 did not exceed 3.6 $cm^3/100$ g, whereas after blowing it increased up to 12 $cm^3/100$ g.

Appreciable absorption of H_2O, CO_2, O_2, and air by liquid glasses was also observed by Slavyanksy /81/. He succeeded in revealing that degassed glass after contact with the enumerated gases bubbles again during subsequent degassing.

Thus, this and a number of other experiments proved that not only H_2O, but also CO_2, SO_2, O_2, and N_2, are being absorbed by glasses. It is true that their solubility, particularly that of N_2, is far lower than that of water vapors. This is also evidenced by the data of Krassikov, and the results of Vargin's and Skobelev's measurements /81/. The latter have found that a barite glass (45% BaO, 13% B_2O_3, 33% SiO_2, 3.5% ZnO, 3% Al_2O_3, 1.6% As_2O_3), at a temperature of 1350°C, contained about 80 cm^3 of gas per 100 g of glass, with the gas consisting of 76-85% H_2O and 9-15% CO_2.

Similar results were obtained /82/ for many sodium-lime glasses. The principal component of the gases (from 42 to 83 $cm^3/100$ g) dissolved in them were water vapors. The share of this component in the products of extraction amounts to 40-97%.

Somewhat different results were obtained by Kondrashova /83/ who

investigated glasses containing B_2O_3(2%) or PBO (10.72%). The total gas saturation of the samples comprised, as usual, 50 - 100 $cm^3/100$ g, but the contents of H_2 (36-67.5%) and N_2 (7-44%) was exceptionally high, while that of H_2O (0.75-4.3%) was small. The results which she produced require additional verification.

Particularly high values for solubility of H_2O in liquid glasses were revealed by Yavoysky. According to his data the contents of H_2O in window glass, at 1250°C temperature and p_{H_2O} = 26 mm Hg, amounts to 0.15%, and in glass designed for chemical vessels - 0.19% (or 236 $cm^3/100$ g) at 1300°C and p_{H_2O} = 35 mm Hg. On the other hand, Karnaukhov and Morozov in a discussion with Yavoysky indicate that with p_{H_2O} = 100 mm Hg no more than 10-20 $cm^3/100$ g, or 0.016 H_2O can dissolve in glass.

We believe this question should also be thrashed out experimentally.

An extraordinary high solubility of water vapors is characteristic for molten K_2SiO_3 which at normal pressure can contain /82/ up to 14 mol. % H_2O (i.e., 1.37% or 2320 $cm^3/100$ g) reducing its melting point approximately by 30°. Solubility of water vapors is also high in $K_2Si_2O_5$(7 mol.% H_2O). It is well to mention here that in the SiO_2 - K_2SiO_3 - H_2O system a number of hydrates ($K_2SiO_3 \cdot 0.5H_2O$; $K_2SiO_3 \cdot H_2O$; $K_2Si_2O_5 \cdot H_2O$; $K_4Si_4O_9 \cdot H_2O$) was revealed, of which the last one melts congruently.

Finally, for $Na_2Si_2O_5$ as well as for K_2SiO_3 the water vapor pressure (up to 140 kg/cm^2) was found /84/ to cause a considerable drop of the melting point (from 850 to 750°C).

Magmas

Natural silicate fusions - magmas - not infrequently contain noticeable quantities of dissolved gases, mainly, water vapors.

Experiments show that granite glass or volcanic glass (~ 75% SiO_2; 14% Al_2O_3; 9% K_2O), for instance, absorb /85/ up to 10% H_2O, at a temperature of 900°C and the pressure of 5000 megabars[1].

Moreover, the conditions of glass crystallization change with increasing H_2O contents, namely a drop of temperature and a rise of pressure are to be registered.

1) 1 megabar - 1.0198 kg/cm^2 - 0.98697 atm.

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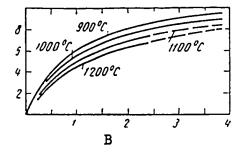

Fig. 146. Effect of pressure and temperature on the solubility of hydrogen in albite.

Legend: A) Solubility of hydrogen, %
B) Pressure, 10^{-3} kg/cm^2

An investigation of the equilibria [85] in the systems $NaAlSi_3O_8$ (albite)–H_2O and $KAlSi_3O_8$(orthoclase)–H_2O conducted under pressures of 3500 kg/cm^2 and at temperatures up to 1200°C also points to a considerable solubility of H_2O. To illustrate this a number of isotherms of S_{H_2O} for molten albite[1] are shown in fig. 146.

In processing these data, Yavoysky [27] arrived at the conclusion that the solubility of water vapors obeys the law of the square root

$$S_{H_2O} = K_{H_2O}\sqrt{p_{H_2O}}. \qquad \text{(VI, 44)}$$

Volarovich and Korchemkin [88] studied the effect of gaseous NH_3, H_2O, N_2, air, and other gases on the crystallization of molten rocks (basalt, diabase, diorite). They disclosed thereby that after passage of H_2O, HCl, HF, and particularly NH_4OH, the viscosity of the melt decreases considerably, a fact which is not observable for N_2 and air. After passing water vapors through crystallized basalt they found up to 0.5% H_2O in it.

At a later date, Volarovich [89] examined the question of H_2O solubility in basalt glass at pressures up to 1000 atm and temperatures attaining 1300°C. It appeared that at 1300°C, for example, and a pressure from 500 to 600 atm the H_2O contents in basalt amounted to about 1%.

S l a g s .

The solubility of gases in slags and the permeability of slags remain,

1) These studies were repeatedly discussed in the periodical literature (see, e.g. [86], [87]).

up to this date, insufficiently studied. Through the efforts, predominantly of the Soviet scientists (Karnaukhov, Morozov, Yavoysky and others), it was established that the widespread opinion of slag as an insulator of metal from gases is wrong. Laboratory and industrial observations show that slags in one or another measure dissolve gases, that they are permeable by gas and can sometimes serve as media for metal degassing.

On the basis of the works of a number of investigators (Chuyko [75], Shatalin [76], Maksimenko [90], and others) the conclusion can be reached that nitrogen is soluble almost in all slags. Its concentration is the greatest in reduction process slags (from electric and blast furnaces) and the least in those of oxidizing processes.

According to Chuyko [75] the concentration of nitrogen attains 0.0633% in white carbide slags containing 0.71% C. According to other data [91] an even higher content of nitrogen (up to 0.23%) is possible in electric furnace slags, whereas in the basic and acid open-hearth slags it is considerably lower and comprises $1 - 3 \cdot 10^{-4}$ and $1 - 3 \cdot 10^{-3}$ % respectively.

In the judgment of Yavoysky [92] the percentage of nitrogen in acid slags is readily determinable. In chilled state they contain 0.0094 – 0.0121% N. The solubility of nitrogen obeys the law of the square root

$$S_N = K_N\sqrt{p_{N_2}}. \qquad \text{(VI, 45)}$$

Moreover, K_N increases with growing temperature faster than in the case of nitrogen solution in iron. Increase of basicity and the replacement of MnO by FeO also contributes to intensification of solubility.

Contrary to the aforesaid, Karnaukhov and Morozov believe that nitrogen does not dissolve in oxidizing slags, since its concentration never exceeds the limits of experimental accuracy. In view of this, it is highly desirable for this matter to be further explored.

The total percentage of hydrogen for acid reduction slags amounts to 12–16 ml per 100 g, and to 7–13 ml/100 g for basic slags, according to certain data [93]. Substantially differing data are recorded by Yavoysky ([92] and others) – the concentration of hydrogen in basic slags is higher than in acid, and reaches in certain cases 50 ml/100 g.

On the basis of his laboratory work Yavoysky [27] came to the following conclusions. The solubility of hydrogen in reduction slags drop with growing temperature. The increase of partial water vapor pressure augments the value of S_H according to equation

$$S_H = K_H\sqrt{p_{H_2O}}. \qquad \text{(VI, 46)}$$

The growth of acid slag basicity involves an increase of solubility. Especially effective in this respect is the addition of CaO, while MnO, MgO, and FeO produce a weaker effect.

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It is interesting to note that the substitution of MnO for FeO causes a rise in hydrogen concentration both in acid and in basic slags, in spite of the decreasing water vapor pressure. It is true that for basic slags a maximum is to be observed. The subsequent lowering of S_H is provoked here by a considerable drop of p_{H_2O}.

Karnaukhov and Morozov, in their polemics with Yavoysky, totally reject the possibility that any kind of relationship could be established for hydrogen solubility in reduction slags versus temperature, composition, and pressure. They assume that the existing methods for the determination of hydrogen contents are too imperfect. Moreover, they state that hydrogen was never found to be present in industrial slags in proportions greater than 0.5-1 $cm^3/100$ g /94/.

In his rebuttal, Yavoysky points out the inadequacy of the measures used against adsorption and the condensation of water vapors in the component parts of the installations utilized for the determination of hydrogen solubility in slags. The underrated results produced by Morozov and Gluskin /94/ are to be attributed, in his opinion, to a possible underestimation of these circumstances.

The problem pertaining to the solubility of hydrogen in slags requires further experimental study.

DIFFUSION OF GASES THROUGH SOLID SILICATES

Influence of Pressure

The investigation of gas diffusion through glasses, carried out by a number authors /95/, revealed that its rate, with a few exceptions, grows linearly with increased pressure drop. From this point of view, the studies by Kondratyev /96/ who accomplished a survey of hydrogen diffusion through quartz are quite interesting.

His apparatus contained two co-axial quartz cylinders. Hydrogen was introduced into the inside cylinder under pressure P. It diffused through the wall into the space between the two cylinders from which gas was evacuated beforehand. The speed of the process was estimated according to the growth of pressure p in this volume.

A few of the plotted curves are recorded in fig. 147. Their numbers correspond in sequence to the order in which the tests were carried out. In the initial period of the first test (curve 1) the inflow of hydrogen was somewhat retarded, but later its pressure changed linearly with time. In the second experiment which followed the first, and was conducted without degassing of the vessel, the linear relationship was registered right from the beginning. The same is generally valid for the third and the fourth tests, carried out at lower pressure. However, the initial section of curve 3 is anomalously characterized by increasing rates of gas ingress.

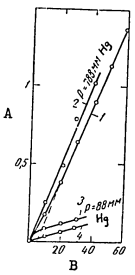

Fig. 147. Variation of the rate of hydrogen diffusion through quartz depending on pressure at 690°C.

Legend: A) Pressure p, mm Hg.
B) Time, min.

The anomalous values of $\frac{dp}{dt}$ at the beginning of both experiments are governed by the critical solubility of hydrogen in quartz glass. During the first test a saturation of quartz takes place which slows down the diffusion process. In the third experiment, on the contrary, it proves to be supersaturated in relation to the decreased pressure. Establishment of a steady distribution of hydrogen along the cross-section of the wall is accompanied by its partial outgassing.

On the basis of the magnitude of the anamolous sections, Kondratyev was able to evaluate the solubility of hydrogen S_H in quartz. Thus, for example, at the temperature of 690°C it proved to be equal to $6 \cdot 10^{-8}$ g/cm^3 for 788 mm Hg and $2.48 \cdot 10^{-8}$ g/cm^3 for 321 mm Hg. In comparing these quantities with the concentrations c_{H_2} of hydrogen in the gaseous phase ($2.63 \cdot 10^{-5}$ g/cm^3 and $1.07 \cdot 10^{-5}$ g/cm^3 respectively), he demonstrated a good conformance with Henry's law.

Actually the ratio of concentrations in both cases is almost identical:

$$\left(\frac{c_{H_2}}{S_H}\right)_{788\ мм} \quad 438: \left(\frac{c_{H_2}}{S_H}\right)_{321\ мм} = 432.$$

Hence, not only the permeability, but also the solubility, of hydrogen in quartz change linearly with pressure. Both these circumstances furnish

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grounds for the belief that hydrogen is in molecular state in quartz.

Indeed, the linear relationship of hydrogen pressure in the external cylinder can be easily deduced should one proceed from the fact of the existence of a proportionality between the solubility of hydrogen and the pressure. Then

$$v = \frac{dc}{dt} = k(C - c) - k'c . \qquad \text{(VI, 47)}$$

Here C and c are hydrogen concentrations in quartz along the edges of the wall;
k and k' are constants.

Moreover, the first item characterizes the diffusion flow through the wall of the internal tube, and the second - through the outer cylinder.

Let us designate, as above, the given pressure of hydrogen in the internal cylinder by P, and the variable pressure in the outer tube - by p. In relation to them the edges of the internal wall are saturated with hydrogen, i.e., C and c are solubilities which are proportional to the pressures.

$$C = aP; \quad c = ap . \qquad \text{(VI, 48)}$$

Whence

$$v = a\frac{dp}{dt} = ka(P - p) - k'ap. \qquad \text{(VI, 49)}$$

Disregarding p, as compared to P, we have

$$\frac{dp}{dt} = kP; \quad p = kPt = k_1 t , \qquad \text{(VI, 50)}$$

i.e., p is proportional to t when P is fixed.

On the other hand, should the passage of hydrogen into quartz be accompanied by dissociation of its molecules into atoms, then its solubility would have to comply with the law of the square root, whereupon

$$C = a\sqrt{P}; \; c = a\sqrt{p} . \qquad \text{(VI, 51)}$$

In substituting these expressions in equation (VI, 47), we obtain

$$v = a\frac{d\sqrt{p}}{dt} = ka(\sqrt{P} - \sqrt{p}) - k'a\sqrt{p} \qquad \text{(VI, 52)}$$

and upon a series of simplifications we find a quadratic, and not a linear,

relationship of p to t

$$\frac{d\sqrt{p}}{dt} = k\sqrt{P}; \quad p = k^2Pt^2 . \qquad \text{(VI, 53)}$$

It should be noted that a linear dependence of the diffusion rate upon pressure is to be observed not only for hydrogen, but also for a number of other gases (He, Ne, N_2, etc.). Moreover, it turns out that hydrogen diffuses less rapidly than helium but faster than nitrogen. This is in good agreement with the ratio of their effective sizes (He - 2.18 Å; H_2 - 2.74 Å; N_2 - 3.75 Å).

To the extent that the structure of quartz is far from being close-packed, the diffusion through it of molecules of some substance or other is not particularly surprising.

Influence of Temperature

Fig. 148 shows that equation (VI, 50) is valid at different temperatures. Moreover, the value of k varies with temperature (fig. 149) according to expression

$$k = k_0 e^{-\frac{9200}{RT}} \qquad \text{(VI, 54)}$$

In other words, the activation energy for molecular diffusion of hydrogen through quartz amounts to 9200 cal/mole, according to Kondratyev.

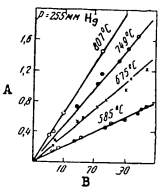

Fig. 148. Effect of temperature upon the rate of hydrogen diffusion through quartz.

Legend: A) Pressure p, mm Hg.
B) Time, min.

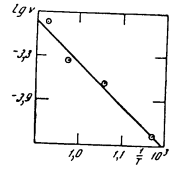

Fig. 149. Curve of the rate of hydrogen diffusion through quartz vs. temperature.

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Close values were produced also by other authors (from 9300 to 12000 cal/mole). Furthermore, the activation energies for other investigated gases are, as a rule, in direct relation to their effective sizes. Thus, for instance, for helium it is smaller (5700 cal), while for nitrogen it is considerably higher (29900 cal) than for hydrogen [95].

Making use of the obtained values of activation energy, Kondratyev produced a theoretical estimate of the coefficient of hydrogen diffusion D through gas. On the basis of expression

$$D = \frac{\delta^2}{\tau}. \qquad \text{(VI, 55)}$$

and replacing

$$\tau = \frac{1}{\nu} e^{\frac{E}{RT}}. \qquad \text{(VI, 56)}$$

we have

$$D = \delta^2 \nu \cdot e^{-\frac{9200}{RT}} \qquad \text{(VI, 57)}$$

Here τ - time of the "sedentary life" of the molecule H_2;

δ - distance apart between the interstices;

ν - frequency of oscillations.

Assuming for quartz $\delta = 3.3$ Å, and $\nu = 10^{12}$ sec^{-1}, he finds that $D \cong 10^{-5}$ cm sec^{-1} for the temperature of 690°C. By order of magnitude this value coincides with the observed value ($1.7 \cdot 10^{-5}$ cm^2 sec^{-1}). This coincidence constitutes an additional substantiation of the molecular state of hydrogen in quartz.

It is important to note that the investigations of other authors [95] show that in the region of low temperatures (< 400°C) a deviation is to be registered from the simple logarithmic rule of the variation of k with T (fig. 150). In particular, at the temperature of 193°C the activation energy of hydrogen diffusion drops to 4300 cal. Analagous deviations were also revealed for He and other gases.

This fact indicates that the character of diffusion processes undergoes substantial changes with decline of temperature. According to Berrer [95] the diffusion of gases through quartz can occur in two ways. One course is via the crystal lattice from interstice to interstice. High activation energy is characteristic for this type of diffusion. It is caused at elevated temperatures by gases with small molecules (H_2, He).

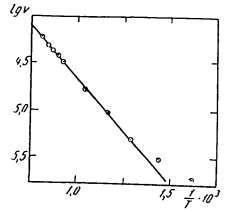

Fig. 150. Effect of temperature on the rate of hydrogen diffusion through quartz.

In the second case diffusion develops following the defects and molecular crevices along the surface of the grains. The transfer of larger molecules (Ar, N_2, O_2) takes place thereby at moderate temperatures.

The cited anomaly may be, probably, explained by the fact that at temperatures higher than 400°C diffusion of hydrogen through quartz develops mainly the first way (inside the grains), and at temperatures below 400°C the second type of diffusion (along the grain boundaries) prevails.

Effect of Glass Composition

Since the molecules of gases shift in the process of diffusion from interstice to interstice, the packing of the structure should diminish the permeability of the solid substance. As is known, the change from quartz to silicates leads to the destruction in the lattice of the largest (diffusion) channels, i.e., makes it more compact. This involves a considerable decrease of the rate of diffusion (or, more precisely, of the constant k).

For example, for He at 300°C temperature, with other conditions being equal [95], the diffusion rate depending on the material of the glass comprises

Quartz	$3.15 \cdot 10^{-9}$
Pyrex	$0.38 \cdot 10^{-9}$
Sodium glass	$0.0098 \cdot 10^{-9}$
Lead "	$0.0037 \cdot 10^{-9}$
Jena "	$0.0036 \cdot 10^{-9}$
Thuringian "	$0.00084 \cdot 10^{-9}$

In summing up, it appears that the diffusion of gases (particularly of He, H_2, Ne) through quartz develops comparatively easily without a change of their molecular state. The absence of any influence of the electric current which passes through glass on the diffusion rate of He and H_2 [97] also speaks in favor of this fact.

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The possibility of such process diminishes during the change from pure quartz (or B_2O_3) to silicates with a more compact structure. Consequently, the molecular permeability of industrial slags seems to be quite low.

THE MODE OF EXISTENCE OF GASES DISSOLVED IN LIQUID SLAGS

The question as to the form of the particles present in liquid slags still remains insufficiently clarified. The high polarity of molten slag or silicate and the relatively close packing of its particles suggest that it is in the form of ions, and not of molecules, that the dissolved gases exist in liquid slags.

Even in solid minerals the dissolution of volatile components usually leads to the formation of OH^-, CO_3^{2-}, Cl^- anions and compound silicon-oxide complexes /98/. Below, we shall consider only the mode of existence of hydrogen and nitrogen.

H y d r o g e n .

Three alternative assumptions were made with respect to the ionic form of hydrogen. Some people believed that it is present in liquid slags in the form of proton H^+ /93/, others thought that it has the form of hydroxyl /17/, /23/, /92/, /99/, the third assumed it to be in both forms - H^+ and OH^- /38/.

A stable existence of a proton in a free form in slag is highly improbable. Its small size and the elementary unit charge produce a considerable potential and lead to very intensive interaction with the surrounding anions /99/.

Since O^{2-} constitutes the main anion-forming component of slag, the proton solidly combines with it into an ion of hydroxyl. Moreover, the linkage occurs either with a free anion of oxygen

$$H^+ + O^{2-} = OH^-.$$

or with a bound anion to form a silicon-oxide (or alumosilicon-oxide) complex.

$$Si_xO_y^{z-} + H^+ \rightarrow Si_xO_{y-1}^{(z-2)-} + OH^-.$$

Thus, the anion of hydroxyl seems to be the most likely form of the existence of hydrogen in liquid slags[1].

This point of view is consonant with the opinions voiced by other authors concerning the structure and properties of hydrogen-bearing silicates. Crystal chemistry teaches that in the lattice of talcum ($Mg_3Si_4O_{10} \cdot 2\,OH$), serpentine ($Mg_3Si_2O_5 \cdot 4\,OH$), hornblende ($(Mg,Fe)_5 Ca_2Si_8O_{22} \cdot 2\,OH$), montmorillonite ($(Mg,Ca)\,Al_2Si_5O_6\,16\,OH$), kaolinite ($Al_2Si_2O_5 \cdot 4\,OH$), muscovite ($(K, Na)\,Al_6Si_6O_{20}\,4\,OH$) and other aluminosilicates (with the exception of zeolites containing molecularly bound water) hydrogen is present in the form of OH /98/.

Analogous considerations were repeatedly expressed in connection with the study of steam adsorption on glasses. Thus, Kysselyov /100/ reports that there exist groups of OH in the adsorption layer which break up as a result of desorption according to the following pattern:

$$\begin{array}{l} -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-OH + OH-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}} \rightleftarrows \\ \rightleftarrows -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O. \end{array}$$

In one of his works, Zhdanov /101/ writes that the presence of OH groups in porous glass, and the decrease of their number upon heat treatment, was convincingly demonstrated by N. G. Yaroslavtzev on the basis of his investigation of infrared absorption spectra.

As concerns the liquid slags directly, one of the experimental evidences which speaks in favor of the presence of OH anions is the direct proportion, revealed by Yavoysky, between S_H and $\sqrt{p_{H_2O}}$ according to equation (VI, 46) as compared to equation (VI, 44). He states that the process of steam solution is accompanied by a breakdown of its molecules

$$H_2O_{(gas)} + O^{2-}_{(slag)} = 2\,OH^-_{(slag)}$$

or

$$H_2O_{(gas} + 2SiO_4^{4-}{}_{(slag)} = 2\,OH^-_{(slag)} + Si_2O_7^{6-}{}_{(slag)}$$

and so on. Similar considerations were expressed also by other authors /98/ with reference to magmas.

By applying the ideal law of mass action as a first approximation to, say, the first of the reactions referred to above, we obtain

$$N_{OH^-} = K\sqrt{N_{O^{2-}}} \cdot \sqrt{p_{H_2O}}, \qquad (VI, 58)$$

whereupon it immediately follows that, with constant composition of slag ($N_{O^{2-}}$ = const), the solubility of water varies with the pressure of its vapors according to the square root law.

1) The possibility is not ruled out of a simple addition of the proton to the complex anions $Si_xO_y^{z-} + H^+ \rightarrow Si_xO_yH^{(z-1)-}$, which, apparently takes place predominantly in highly acid slags.

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Furthermore, Yavoysky [2] demonstrated that the experimental plots for N_{OH^-} include not only $\sqrt{p_{H_2O}}$, but also $\sqrt{N_{O^{2-}}}$. Thus, for a four-component slag (CaO, FeO, MnO, SiO_2) he obtained an equation

$$N_{OH} = \{[7.22 + 1.26]\sqrt{N_{O^{2-}}}\}10^{-1} - 0{,}81 \cdot 10^{-5}(t - 1370°)\}\sqrt{p_{H_2O}}. \qquad \text{(VI, 59)}$$

It further appears that during the extraction of gases from slags it is water, and not hydrogen, that evolves (as is also the case during the desorption of H_2O from glass). Moreover, hydrogen, as compared to water, is considerably less soluble in molten silicates and slags which do not contain easily reducible oxides (FeO, MnO). This also conflicts with the theory concerning the presence of H^+ protons or even free atoms of hydrogen.

It is necessary to remark that only through admission of the existence of hydroxyl anions it becomes possible to explain the observed dependence of hydrogen solubility upon the composition of slag. Indeed, the greater is the basicity of the latter, the higher is the activity or concentration of oxygen ions which leads, according to equation (VI, 58), to a growth of hydrogen solubility.

Furthermore, the process of water vapor solution in slag consists in its interaction with the anion of oxygen. The activity of the latter does not depend only on the concentration, but also on the interaction energy with the surrounding cations. The greater is their charge and the smaller their size, the more stable become the bonds of the oxygen ions, and the more difficult becomes the process of slag hydration.

Consequently, the replacement of cations Fe^{2+} by Mn^{2+}, and even more so by Ca^{2+}, intensifies the activity of O^{2-} anions, which shifts the equilibrium of reaction $H_2O + O^{2-} = 2\,OH^-$ towards an increase of hydroxyl concentration. Particularly strong, from this standpoint [102], must be the increase of H_2O solubility in slag upon the introduction into it of large Na^+, K^+, cations, i.e., alkali metal oxides.

Finally, the capillary activity of hydrogen, reported by Yavoysky, could also serve as an argument in favor of the OH^- anion. It can be explained by the fact that the weaker OH^- anions (as compared to O^{2-} and SiO_4^{4-}) are being driven off towards the slag-gas interface. Had hydrogen been in the form of proton, it would have not been able to reduce surface tension. In this case it would not have been hydrogen, but the less powerful cations, that would have been expelled into the surface layer.

However, Yavoysky's conclusion concerning the capillar activity of hydrogen was made exclusively on the basis of the spreading out of a drop of slag after introduction of water vapors from the outside. He failed to take into account the change of surface tension at the solid body-gas

interface.

Meanwhile Slavyansky [81] showed that the spreading of silicates over platinum is related not so much to the presence of CO_2, H_2O, H_2 and N_2, as to O_2 which forms oxide films with Pt and Ir. These results contradict Yavoysky's conclusions and it is deemed that in view of this fact this problem should be made subject to further examination.

Nitrogen.

No sufficiently reliable data are available at the present time for the judgment of the move of nitrogen existence in liquid slags. Moreover, as noted by Trubin [60], even the studies concerning the solubility of N_2 in melts are still in the embryonic state. Yet, it still seems worthwhile to record the considerations expressed by individual authors in order to stimulate further investigations into this matter.

In Chuyko's opinion [59], of the two combinations - $CaCN_2$ and Si_3N_2 - possible for nitrogen in slag, preference should be given to the first, because the second is subject to energetic decomposition by iron, which eliminates the chance of its existence in the bath of an arc furnace.

Maksimenko [90], on the contrary, categorically denies the existence of $CaCN_2$ in molten slag on the basis of the commonly known thermal instability of cyanamide which decomposes at high temperature according to the following pattern

$$CaCN_2 + CO \rightarrow CaO + 2C + N_2.$$

Referring to other investigators [103], he considers it to be more probable[1]) for calcium azide (Ca_3N_2) to form in slag. It is a thermally stable compound and is commonly present as an impurity in commercial calcium carbide (CaC_2).

It should be noted, however, that CaC_2 and $CaCN_2$ form a low-melting eutectic by virtue of which fact a complete thermal decomposition of $CaCN_2$ up to CaC_2 is not feasible by normal methods [105]. Moreover, even a step-by-step process does not assure [106] the derivation of a product containing more than 99% CaC_2. $CaCN_2$ is always contained in carbide as an unavoidable impurity.

It is true that in the conditions prevailing in electric furnaces the CN_2^{2-} ion partially changes into other anions under the influence of excess calcium, namely into CN^-, N^{3-} or even (in the presence of hydrogen) into NH^{2-}. Yet, these reactions develop incompletely, in view of which fact

1) A similar point of view is shared by Edneral [104].

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there always are admixtures of calcium cyanamide and calcium azide in commercial carbides. The solubility of calcium azide in molten slags has not yet been investigated.

Thus, it appears to be possible to expect to find the following nitrogen-bearing anions - CN_2^{2-}, CN^-, and N^{3-} - in highly basic, and particularly in carbide slags. Moreover, taking into account Yavoysky's observation (which still calls for additional verification) that the solubility of nitrogen in slags obeys the law of the square root, it would seem that preference should be given to the groups with one atom of N, i.e., to the anions CN^- and N^{3-}.

The mode of nitrogen's existence in acid and semi-acid slags is absolutely unclear. Reference is usually made to the solubility of nitrides, carbonitrides and cyanamides in them but without sufficient substantiation to this effect.

Experiments show [107] that the contents of nitrogen in blast furnace slags grows regularly with increasing silicon and manganese percentage in cast iron. This, of course, does not imply that nitrogen dissolves in slag in the form of silicon nitrides (1) because the latter are very easily decomposed by iron. It is most probable that "more deoxidized" slags are produced in these conditions, in which the stability of CN_2^{2-}, CN^-, and N^{3-} anions increases. The cited anions are known to be easily oxidized; it is probably because of this that the nitrogen contents in the oxidizing slags is small [91].

4. DISTRIBUTION OF HYDROGEN BETWEEN SLAG AND METAL.

The problem of hydrogen distribution between the liquid phases of a heat began to attract the attention of metallurgistis, especially after it became clear that slag is capable of dissolving measurable quantities of gases and is, therefore, permeable to them.

The first and unsuccessful attempt to establish the quantitative regularities for hydrogen, on the basis of electrochemical concepts, was made [93] on the erroneous premises that hydrogen is present in slag in the form of proton. In recording the reactions between metal and slag

$$2H^+_{(slag)} + Fe_{(met)} = Fe^{2+}_{(slag)} + 2H_{(met)},$$

$$2H^+_{(slag)} + Mn_{(met)} = Mn^{2+}_{(slag)} + 2H_{(met)}$$

the authors obtained an expression for the equilibrium constants

$$K_{H.Fe}\frac{|H|\sqrt{(Fe^{2+})}}{(H^+)};\ K_{H.Mn}=\frac{|H|\sqrt{(Mn^{2+})}}{(H^+)}. \qquad (VI, 60)$$

In elaborating the data of the industrial heats, they determined also the temperature dependences for K, for example,

$$K_{H.Mn} = 3{,}97 - 0{,}0164(t - 1550). \qquad (VI, 61)$$

The most essential errors of this work are the inferences concerning the proton form of hydrogen in slags and the existence of equilibrium in the conditions of industrial heats.

A more deliberate approach to the analysis of this problem was made by Yavoysky [27]. First of all he applied the so-called method of gradual elimination [108] for the evaluation of the equilibrium conditions from the investigation data of the commercial heats. The essence of this method consists in the simultaneous determination not only of the metal and slag compositions but also in establishing the direction of the process. In this particular case it became clear which one of the phases is supersaturated with hydrogen in relation to the other. Knowledge of the manner of the change of the supersaturation sign (direction of the arrow in the diagram) permits estimation of the conditions of equilibrium.

Furthermore, Yavoysky proceeded from a more reliable assumption that hydrogen exists in slag in the form of hydroxyl and admitted the presence in basic slag of the following anions:

$$FeO_2^-,\ CrO_2^-,\ AlO_2^-,\ OH^-,\ O^{2-},\ PO_4^{3-}\ \text{и}\ SiO_4^{4-}.$$

In view of this the interation between the metal and slag will proceed according to the following reactions:

$$2OH^-_{(slag)} + Fe^{2+}_{(slag)} = Fe_{(met)} + 2O_{(met)} + 2H_{(met)},$$

$$2OH^-_{(slag)} + Mn^{2+}_{(slag)} = Mn_{(met)} + 2O_{(met)} + 2H_{(met)}$$

the equilibrium constants of which may be recorded as

$$K_{Fe.H} = \left\{\frac{(OH^-)}{|O|\,|H|}\right\}^2 \frac{(Fe^{2+})}{|Fe|},$$

$$K_{Mn.H} = \left\{\frac{(OH^-)}{|O|\,|H|}\right\}^2 \frac{(Mn^{2+})}{|Mn|}. \qquad (VI, 62)$$

Here the parenthesized values represent the ion fractions of slag, calculated on the basis of the theory of perfect ionic solutions [109].

In computing the value of K on the basis of the a priori non-equilibrium concentrations and using the methods of gradual elimination, he

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determined graphically (fig. 151) the equilibrium constant and its dependence on the temperature. Thus for the reaction with the participation of Fe^{2+} it follows that

$$\lg K_{Fe.\ H} = \frac{25\,800}{T} - 13{,}4, \qquad \text{(VI, 63)}$$

and for Mn^{2+}

$$\lg K_{Mn.\ H} = \frac{42\,200}{T} - 19{,}2. \qquad \text{(VI, 64)}$$

Yavoysky remarks that the low accuracy of the determination of (OH^-), $\angle H \rangle$, and $\angle O \rangle$ concentrations gives an orientation character to the recorded relationships, and assumes that the possible deviation from the real values may be 10 to 20-fold.

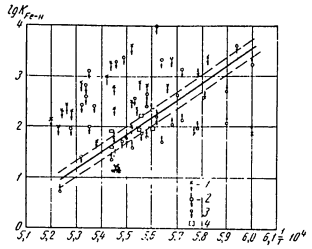

Fig. 151. Dependence of $\lg K_{Fe}$ upon temperature:

1 - 185-350 ton capacity open-hearth furnaces; 2 - treatment of slags in the ladle; 3 - small open-hearth and electric furnaces; 4 - heats run in induction furnace.

As it may be seen from equations (VI, 63) and (VI, 64) rising temperature involves a drop of the equilibrium constant values, which is equivalent (see equation (VI, 62)) to the increase of hydrogen contents in metal. This conclusion is in conflict with the deduction which follows from the formulas (VI, 60) and (VI, 61). Indeed, according to relationships (VI, 60) and (VI, 61) the growth of temperature reduces K and $\angle H \rangle$ which, apparently, contradicts the facts.

It may appear at first glance that a singular result follows from the expressions for the equilibrium constants, proposed by Yavoysky, namely, that the greater is the oxidizing power of the slag (for example, the greater is the concentration of Fe^{2+}) the higher is the contents of hydrogen in metal. Yet this is not so.

Account must be taken of the fact that the Fe^{2+} ions "accompany" the passage into metal not only of the anions OH^-, but also of O^{2-}, i.e.,

$$Fe^{2+}_{(slag)} + O^{2-}_{(slag)} = Fe_{(met)} + O_{(met)}.$$

The exclusion from the equilibrium constant of this passage

$$K_{Fe.\ O} = \frac{|O|\,|Fe|}{(O^{2-})(Fe^{2+})} \qquad \text{(VI, 65)}$$

of the quantity $\angle O \rangle$ by means of the expression for $K_{Fe,H}$ produces

$$K = \frac{(OH^-)^2\,|Fe|}{(O^{2-})^2(Fe^{2+})\,|H|^2}. \qquad \text{(VI, 66)}$$

The relationship between (O^{2-}) and (OH^-) is established by the process

$$H_2O_{(gas)} + O^{2-}_{(slag)} = 2OH^-_{(slag)},$$

for which

$$\frac{(OH^-)^2}{(O^{2-})\,p_{H_2O}} = K'. \qquad \text{(VI, 67)}$$

From equations (VI, 66) and (VI, 67) we find

$$\frac{p_{H_2O}}{(Fe^{2+})(O^{2-})\,|H|^2} = K'', \qquad \text{(VI, 68)}$$

or

$$a_{FeO}[H]^2 = K'''p_{H_2O}. \qquad \text{(VI, 69)}$$

This relationship shows, as one could have well expected, that the increase of FeO activity in slag reduces the concentration of hydrogen in metal (if the temperature and the contents of water vapors remain constant). Thus the contradiction referred to above proves to be only an apparent one.

On the other hand, one should bear in mind the following: The total absence in slag of Fe^{2+} or Mn^{2+} ions hinders the passage both of oxygen and OH^- into the metal, i.e., the concentrations of $\angle O \rangle$ and $\angle H \rangle$ will in this case be equal to zero. And conversely, according to equations (VI, 60) and (VI, 61), the absence in slag of Fe^{2+} and Mn^{2+} cations does not present an obstacle to the saturation of metal with hydrogen.

Upon rewriting the expression (VI, 68) or (VI, 69) as follows

$$a_{Fe^{2+}} \cdot [H]^2 \cdot a_{O^{2-}} = \text{const}, \qquad \text{(VI, 70)}$$

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we note that the greater is the activity of the oxygen ion in slag, the lesser is the hydrogen contents in metal, provided all other conditions are equal. In other words, the outgassing effect of slag will be the more significant, the higher is its basicity and the greater is the number in it of the large cations with small charges (for example, N^+ or K^+).

This conclusion was checked by Yavoysky, Geld and Serebrennikov [23] on liquid ferro-alloys in industrial conditions by means of additions of crushed glass into the runner or under the stream of metal. As it may be seen from fig. 152, the admixture of this material, so rich in Na^+ ions, leads in all cases to the reduction of the hydrogen contents in the alloys.

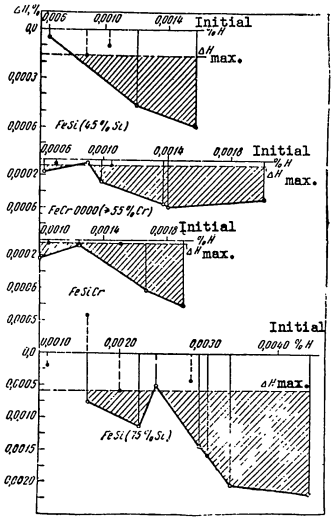

Fig. 152. Dependence of the degree of metal outgassing by glass upon the contents of hydrogen in metal.

Dotted horizontal lines - limits of degassing without glass additions.

Let it, finally, be noted that the investigation of the kinetics of the process in production conditions, has led Yavoysky to the conclusion that the process of hydroxyl penetration into the metal is characterized by high activation energy. In other words, the main barrier which impedes the transfer of hydrogen is concentrated at the surface of the slag-metal boundary.

In favor of this conclusion also is the high value of the bonding energy of hydrogen and oxygen in OH^-. Rupture becomes possible, probably, only under the influence of the atoms of iron in the surface layer of the metal. For this reason, the total reaction of transfer should, it seems, be considered as consisting of at least two stages:

$$2OH^-_{(slag)} + Fe_{(met)} = Fe^{2+}_{(slag)} + 2O^{2-}_{(slag)} + 2H_{(met)}$$
$$+$$
$$2Fe^{2+}_{(slag)} + 2O^{2-}_{(slag)} = 2Fe_{(met)} + 2O_{(met)}$$
$$\overline{2OH^-_{(slag)} + Fe^{2+}_{(slag)} = Fe_{(met)} + 2O_{(met)} + 2H_{(met)}}$$

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Chapter VII.

ON THE MODE OF METALLOID EXISTENCE IN DISSOLVED METALS.

The problem concerning the character of bonds between the atoms of metal and the metalloids dissolved in it — in spite of its great importance for metallurgy — still remains among those least of all elaborated. This is partially due to the complexity of the problem as well as to the fact that most of the attempts at its solution were based solely on thermodynamic data. Such one-sided characteristic of the system, naturally, enables only a partial identification of the individual moments of the subject under survey.

It was only in very recent times that structural and kinetic data relative to certain elements dissolved in metal were revealed in investigations carried out primarily by metallophysicists and metallographers.

Only the general regularities are considered below which permit drawing certain conclusions on the forms of the dissolved elements. As to the basic factual material covering the interaction of metal and slag with gases, this was discussed in chapter VI.

I. EQUILIBRIA BETWEEN GAS AND METAL

DIATOMIC GASEOUS ELEMENTS

The interaction of diatomic gas (G_2) with metal (Me), as a rule with iron, may be represented by the following scheme[1]:

$$y\,\underline{Me} + x\,G_2 = \underline{Me_y G_{2x}}. \qquad \text{(VII, a)}$$

At minor pressures and small solubility of gas, the equilibrium constant is equal to[2]

$$K = \frac{a_{\underline{Me_y G_{2x}}}}{a_{Me}^{y} \cdot a_{G_2}^{x}} \cong K_1 \frac{[G_{2x}]}{p_{G_2}^{x}}. \qquad \text{(VII, I)}$$

Hence

$$p_{G_2}^{x} = K' [G_{2x}]. \qquad \text{(VII, 2)}$$

Consequently the solubility of diatomic gas (H_2, O_2, N_2, and so on)

1) The designations of those substances which form solutions with metal are underlined.

2) Brackets are used to denote the concentrations of corresponding substances dissolved in metal.

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in metal is proportional to its pressure in the x power.

The magnitude of x, determined experimentally, enables certain conclusions to be made concerning the mode of existence of the dissolved gas. Indeed, if x = 1, then equation (VII, 1) corresponds to Henry's law, and, consequently, unit cells containing two atoms of G_2 must exist in metal as well as in gas. On the contrary, fractional values of x point to a different type of Me_yG_{2x} structure.

Experimental studies of the solubility isotherms of hydrogen, nitrogen and other gases, carried out, for example, by Chizhevsky, Zhukov, Sieverts, Yavoysky, Karnaukhov, and Morozov (see, e.g., /1/) showed that $x = \frac{1}{2}$, i.e.,

$$p'_{G_i} = K'[G]. \qquad \text{(VII, 3)}$$

Karnaukhov and Morozov /2/, in particular, found $x = \frac{1}{2}$ (fluctuations from 0.46 to 0.50) for hydrogen in liquid iron at 1585 ± 15°C.

The validity of the square-root law permits the belief that gases dissociate during dissolution and produce with metal groups which contain one atom G, i.e., Me_yG. On the basis of this regularity it is impossible to say anything more about the solutions under consideration. As a matter of fact, the question pertaining to the magnitude of y[1]) remains quite open. Besides, it is impossible to give preference to anyone of the three states of G: ionic, atomic or molecular[2]). In other words, it is impossible to establish the character of the forces of interaction between the atoms of Me and G.

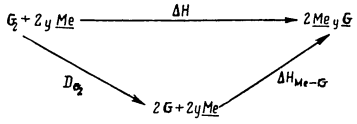
This circumstance is usually bypassed in technical literature under the conditional assumption that gases, which produce stable compounds in the solid state with metals $(MeG)_{solid}$, dissolve in them in the form of molecules of these compounds (FeO, MnO, FeS, and so on). On the other hand, for hydrogen, which forms unstable hydrides with ferrous metals, an atomic form is sometimes assumed as possible.

Incidently, some investigators /3/ to this day insist persistently on the erroneous assumption pertaining to the existence of FeH hydride in liquid iron.

Additional data could be obtained through analysis of the solubility isobars by means of which the thermal effect ΔH is being determined. The solubility of diatomic gases in a number of metals increases with growing temperature, indicating the endothermic character of the process (e.g., see /4/).

Inasmuch as the interaction of the Me and G atoms is strong and the initiation of the interaction process should be accompanied by release of heat ($\Delta H_{Me-G} < 0$), while the bonds between the molecules of G_2 in gas are weak, it is reasonable to expect that there should be a stage in the process of solution during which a considerable proportion of the energy ($D_{G_2} > 0$) should be consumed.

In conjunction with the aforesaid, the dissociation of G_2 molecules into atoms - which takes place at the surface of the metal and is facilitated by its force field - should constitute this stage. Indeed, as it may be seen from the following cycle



the value of $\Delta H = \Delta H_{Me-G} + D_{G_2}$ will be positive only when

$$|D_{G_2}| > |\Delta H_{Me-G}|.$$

Thus, the recorded experimental regularities of thermodynamic nature (effect of p_{G_2} and T) lead to the conclusion that the solution of certain gases in a number of metals is accompanied by a disintegration of their molecules into atoms and the formation of groups containing one G atom.

However, on the basis of these data it is impossible to determine either the form of the gas atom, or the character of the bonds by which it is linked to the metal atoms. One can merely state that the energy of interaction of yMe with G is great. Thus, for H_2 the heat of solution in iron ΔH was experimentally determined to be equal to 15000 - 16000 cal/mole. Considering that D_{H_2} amounts to 101000 cal we obtain

$$\Delta H_{FeH} = -D_{H_2} + \Delta H = -101\,000 + 15\,000 = -86\,000 \text{ cal/mole}$$

1) It should be borne in mind that, unlike gases, where a small number of atoms constitutes a molecule, each particle in condensed substances interacts with all other particles. Consequently, strictly speaking, the atom of the dissolved metalloid interacts with all N ions of metal, i.e., y = N. However, by way of first approximation, it becomes possible to speak of the number of metal ions pertaining to each G atom, taking into account only those of them whose interaction with G is stronger than that of the others.

2) Comprising the groups, within the bounds of which homeopolar bonds are prevalent.

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In those cases when $|\Delta H_{Me-G}| > |D_{G_2}|$, an exothermic process will take place, and the solubility of G_2 will drop with the rise of temperature. Such, for instance, is the condition in systems H_2 - k, Na, Ca, Zr, etc.

COMPOUND GASES.

Certain information pertaining to the mode of sulphur and oxygen existence (G = S , O) is provided by investigations of the equilibria of metal with gases of a more complex composition:

$$\underline{Me, G} + H_2 = \underline{Me} + H_2G. \qquad \text{(VII, b)}$$

Let us assume that this interaction is reflected in the following stoichiometric scheme

$$y\,Me + x\,H_2G = Me_y G_x + x\,H_2. \qquad \text{(VII, c)}$$

By simplifying the expression for the equilibria constant relative to small pressures and dilute solutions, we obtain

$$K = \frac{a_{Me_y G_x} \cdot f^x_{H_2}}{a^y_{Me} \cdot f^x_{H_2G}} \cong [\%G]\left(\frac{p_{H_2}}{p_{H_2G}}\right)^x, \qquad \text{(VII, 4)}$$

or

$$\left(\frac{p_{H_2G}}{p_{H_2}}\right)^x = K_1[\%G], \qquad \text{(VII, 5)}$$

where [%G] is the contents of gas in metal expressed in percent by weight.

In comparing this expression with the experimental data it is possible to determine x. Thus, for instance, a study of equilibrium during oxidation of liquid iron by steam /5/ showed that there is a rectilinear relationship between $\frac{p_{H_2O}}{p_{H_2}}$ and [% O] (or [%F O]).

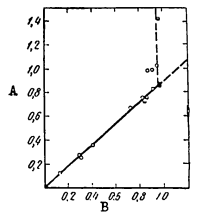

Fig. 153. $\left(\frac{H_2O}{H_2}\right)$ gas composition versus FeO concentration in metal.

Dotted line - conditions of iron saturation with oxygen.

Legend: A) Composition of gas $\frac{H_2O}{H_2}$

B) Contents of FeO, %

The results established at the temperature of 1600°C are recorded in fig. 153. For the system under survey x = 1, which implies that oxygen is monatomic when it is found in some association or other with particles of iron.

Of course, such investigations do not yield information pertaining to the coordination number of oxygen in metal, nor on the magnitude of y. Like the preceding data they fail to shed light on the very important question concerning the nature of the Me-G bonds.

Analysis of the interaction of hydrogen with liquid iron containing a relatively small proportion of sulfur, disclosed /6/ that direct proportionality is also to be observed between $\frac{p_{H_2S}}{p_{H_2}}$ and [% S], i.e., that x in this case is also equal to 1. This bespeaks the monatomic character of gas in structural complexes with iron.

The behavior of sulfur and oxygen in non-ferrous metals is discussed in the works by Vol'sky and his collaborators /7/. Thus, in cooperation with Slobodsky /8/, he investigated by indirect method the equilibrium

$$2\,\underline{Cu} + CO_2 = \underline{Cu_2O} + CO. \qquad \text{(VII, d)}$$

It transpired thereby, that, calculated on the basis of their data, the partial pressures p_{O_2} over the solutions of Cu_2O in liquid copper, at

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the temperature of 1100°C, obey the mass action law in its ideal form (see fig. 154). In other words, the observed values of p_{O_2} are in fair agreement with those calculated on the basis of equation

$$p_{O_2} = K\frac{[Cu_2O]^2}{[Cu]^4} \cong K'[Cu_2O]^2 = 10^{-6,76}\,[Cu_2O]^2. \qquad \text{(VII, 6)}$$

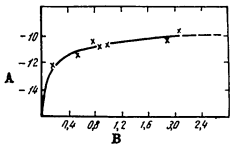

Fig. 154. Dependence of the elasticity of Cu_2O dissociation on its concentration in metal at 1100°C.

The curve is plotted according to equation (VII, 6). The points represent indirect measurement data.

Legend: A) lg P_{O_2} atm.
B) Cu_2O contents, mol %.

However, since the percentage of Cu_2O did not exceed 2.09 mol %, it cannot be replaced by oxygen concentration, whereupon

$$p''_{O_2} = K_1[O]. \qquad \text{(VII, 7)}$$

Thus, experiments confirm only the fact that oxygen in grouping with copper is monatomic.

Analogous results were also obtained for the equilibrium

$$\underline{PbS} + H_2 = \underline{Pb} + H_2S. \qquad \text{(VII, •)}$$

The elasticity of PbS dissociation upon solution in liquid Pb conformed to the equation of the ideal law of mass action

$$p_{S_2} = 10^{-3,56}\frac{[PbS]^2}{[Pb]^2}. \qquad \text{(VII, 8)}$$

However, the system Pb-PbS is known to have a region of separation into two liquids which begins with small concentrations of S. Consequently, positive deviations from the law of ideal solutions should be expected in this region. In compliance therewith, the equilibrium between gaseous sulfur S_2 and that dissolved in lead S, should be more correctly recorded as follows

$$\underline{S} = \frac{1}{2}S_{2\,(gas)}, \qquad \text{(VII, f)}$$

whence

$$a_S = Kp''_{S_2}, \qquad \text{(VII, 9)}$$

or

$$\frac{a_S}{a_S^0} = \left(\frac{p_{S_2}}{p^0_{S_2}}\right)^{1/2}. \qquad \text{(VII, 10)}$$

According to the equilibrium values of p_{S_2} over Pb-PbS melts determined by Vol'sky and Slobodsky, the activity was calculated for sulfur by means of equation (VII, 10). The activity was considered thereby to be equal to the atomic fraction of the most diluted solution. In the given case $a_S^0 = N_S^0 = 0.023$.

The activity coefficients, thus calculated [97], appeared to be smaller than unity and fluctuated irregularly from 1 to 0.46. Similar results are to be registered in investigations of the given melts by other experimental procedures, namely by the method of electromotive forces [97]. Yet, the activity coefficients in this case exceeded unity (1.00 - 1.26).

In the studies made by Vol'sky and Agrachyova [77], the following equilibria were investigated

$$\underline{FeS} + H_2 = \underline{Fe} + H_2S, \qquad \text{(VII, g)}$$

$$\underline{NiS} + H_2 = \underline{Ni} + H_2S. \qquad \text{(VII, h)}$$

Here the concentration of the melt components varied over a wider interval, and the contents of sulfur considerably exceeded that registered in the Pb-PbS system.

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As one should have expected, there proved to be no complete agreement here with the ideal law of mass action, moreover in the first case the deviations were somewhat smaller than in the second. In explaining this, Vol'sky and Agrachyova advance the assumption of a partial dissociation of iron sulphide with the formation of diatomic sulfur in the melt

$$2\,\underline{FeS} = 2\,\underline{Fe} + \underline{S_2}.$$

This, of course, seems to be highly improbable, considering the fact that, according to their own calculations, the concentration of such sulfur amounts to approximately 0.6% in pure FeS at 1200°C.

Finally, in order to reconcile the data pertaining to the Ni - S melts with the ideal law of mass action, they are compelled to assume the simultaneous existence and partial dissociation of two sulphides (NiS and Ni_3S_2).

Thus, they are apt to consider the coincidence with or the divergence from the ideal law of mass action as the sole criterion of validity for one or another hypothesis concerning the existence modus of the element dissolved in metal. In doing so, they disregard the other reasons which might also influence the variability of the activity coefficient of the component in the melt. Listed among these reasons could be varying degrees of ordered or disordered arrangement of particles which, however, do not lead to the formation of molecules.

In one of his works, Gerassimov /10/ chose to take the course of compromise. He took both the existence of molecules as well as the non-ideal nature of the solution into account.

While investigating the equilibrium of the Bi_2S_3-Bi melts with hydrogen, he established that the assumption concerning the existence of Bi_2S_3 molecules encounters obstacles. The quantity K_1 amounting to

$$K_1 = K\frac{\gamma_{Bi_2S_3}}{\gamma^2_{Bi}} = \frac{[Bi]^4}{[Bi_2S_3]}\left(\frac{p_{H_2S}}{p_{H_2}}\right)^3, \qquad \text{(VII, 11)}$$

does not tend to a constant value during passage into dilute solutions, where γ_{Bi_2} and $\gamma_{Bi_2S_3}$ are close to unity.

Yet in assuming the existence in the melt of BiS molecules, i.e., the existence of equilibrium

$$\underline{BiS} + H_2 = \underline{Bi} + H_2S, \qquad \text{(VII, 1)}$$

one finds that the above requirement is fulfilled. With small percentages of sulfur the quantity K_2 equal to

$$K_2 = \frac{[Bi]\,p_{H_2S}}{[BiS]\,p_{H_2}}, \qquad \text{(VII, 12)}$$

is constant, while the activities of bismuth and sulfur correspond to their concentrations (fig. 155).

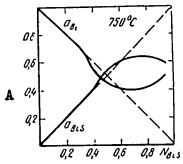

Fig. 155. Effect of the Bi-BiS system composition on the activity of the components at 750°C.

Legend: A) Activity, a_i

Whereupon a conclusion may be drawn that diluted solutions contain sulfur in the form of BiS molecules.

However, since equation (VII, 12) is valid for greater percentages of bismuth (/Bi/ $\longrightarrow$ 1), it can be modified to assume the aspect of

$$p'_{S_2} = K'[BiS] = K''[S]. \qquad \text{(VII, 13)}$$

To put it in a different way, the experimental data, just as before, simply indicate that monatomic groups seem to constitute the most probable form of existence of sulphur in the melt.

Similar conclusions result from the data pertaining to the interaction of liquid metals with complex gases, the solution of which is accompanied by the penetration into the metal not of a single one but of a number of their constituents.

The systems of copper-sulfurous gas and iron-carbon monoxide can serve as examples thereof.

According to the available data /11/ the solubility of sulfurous gas in copper is not too accurately described by the law of square root; the points fitting better a straight-line with the coordinates: solubility - cube root of sulfurous gas pressure. However, the straight line produced thereby does not pass through the origin of coordinates.

This, apparently, is to be ascribed to the insufficient accuracy of the mentioned experimental data. Actually, it was demonstrated later on /12/ that the solubility of sulfurous gas in pure copper grows rectilinearly

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with $\sqrt[3]{p_{SO_2}}$ of very small pressures (fig. 130). This regularity indicates that a dissociation of molecules into atoms takes place during the solution of sulphurous gas in copper, according to equation

$$SO_{2\,(газ)} = \underline{S} + 2\underline{O}, \qquad \text{(VII, j)}$$

whence

$$K \cong \frac{[S]\,[O]^2}{p_{SO_2}}, \qquad \text{(VII, 14)}$$

$$[SO_2] = K' \sqrt[3]{p_{SO_2}}.$$

As one should have expected, the solubility of sulfurous gas in copper containing considerable amounts of sulfur conforms, according to the same data, to the square-root law, since in this case (S) $\cong$ const.

Experimental studies of the CO equilibrium with liquid iron, so important for the technology of ferrous-metals, were conducted by a series of investigators. In particular, in one of the works /13/ the pressure of CO during tests was observed to vary from 1 to 20 atmospheres. By comparison of the results produced with the expressions for equilibrium constants, activity coefficients for carbon and oxygen dissolved in metal were determined.

Thus it appeared, for instance, that the ratio $\frac{p_{CO}^2}{p_{CO_2}}$ varies linearly with the concentration of carbon, if it does not exceed 0.5%.

Having recorded for the reaction

$$\underline{C} + CO_2 = 2CO \qquad \text{(VII, k)}$$

the equilibrium constant as

$$K_1 = \frac{p_{CO}^2}{p_{CO_2}[C]\,\gamma_C} = \frac{K_1'}{\gamma_C}, \qquad \text{(VII, 15)}$$

one may assume that the value of γ_C can be considered equal to unity within the mentioned range of carbon contents, while $K_1 = 430$ (at 1540°C). For any other (C) the value of γ_C differs from 1 and is determined from the relationship

$$\gamma_C = \frac{K_1'}{430} = \frac{p_{CO}^2}{p_{CO_2}[C] \cdot 430}. \qquad \text{(VII, 16)}$$

Similarly for the reaction

$$\underline{O} + CO = CO_2 \qquad \text{(VII, l)}$$

the value is being sought out for the equilibrium constant

$$K_2 = \frac{p_{CO_2}}{p_{CO}[O]\,\gamma_O} = \frac{K_2'}{\gamma_O} \qquad \text{(VII, 17)}$$

with respect to small carbon concentrations. It is being assumed thereby that $\gamma_O \to 1$, if (C) $\to$ 0. Upon determination of K_2 for this case to be equal to 1.21, calculation is made of the activity coefficient for oxygen as per equation

$$\gamma_O = \frac{K_2'}{1{,}21} = \frac{p_{CO_2}}{p_{CO}[O] \cdot 1{,}21}. \qquad \text{(VII, 18)}$$

Computations show that with increasing carbon concentration its activity coefficient grows to exceed unity. On the contrary, γ_O decreases considerably and continuously.

The cited authors are apt to ascribe these deviations of the melt properties from the laws of ideal solutions to the existence in the liquid phase of chemical compounds of Co and Fe_3C (or more complex carbides). Moreover, the main role in the drop of γ_O and the growth of γ_C is attributed by them to the formation of carbon monoxide. The solubility of the latter in the form of molecules in iron at a temperature of 1540°C is assumed by them to be equal to 0.0028 p_{CO}. The above-mentioned permits them to write for the reaction

$$\underline{C} + \underline{O} = CO_{(газ)} \qquad \text{(VII, m)}$$

the following expression for the equilibrium constant:

$$K_3 = \frac{p_{CO}}{[C]\,\gamma_C\,[O]\,\gamma_O} = \frac{p_{CO}}{([C] - 0{,}0012\,p_{CO})([O] - 0{,}0016\,p_{CO})}. \qquad \text{(VII, 19)}$$

The constancy of the K_3 values, thus calculated, is considered as serving to confirm the existence of CO molecules in liquid iron.

This conclusion, however, hardly corresponds to reality. Certain inaccuracies and even contradictions between the experimental data of these investigators should be underlined in the first place. This was first noted by Stark /14/. In a critical analysis of the experimental results, he points out the absence of justiable grounds for the inference concerning the existence in metal of CO molecules in noticeable concentration.

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Rather, it is more reasonable to expect that carbon monoxide, like H_2, N_2, SO_2, O_2 and other gases, dissociates during solution in iron into atoms which form some form of structural group in conjunction with the particles of metal. Indeed, the compact packing of the iron atoms (coordination number 12) does not permit the relatively large CO molecules to distribute themselves in the lattice (apparently, also in liquid iron) without considerable deformation. Most probably they break up into carbon and oxygen atoms.

On the other hand, Temkin and Schwartzmann [15] believe that the observed increase of γ_C following the growth of carbon concentration in iron is related to the formation of solutions of the intrusion type. Departing from the fact that the lattice of gamma-iron is face-centered cubic, and that the atoms of carbon are distributed in it in the centers of the cubes, they argue that for ν_1 atoms of Fe there should be $\frac{1}{4}\,\nu_1$ sites available for atoms of C[1].

If the true number of carbon atoms amounts to ν_2, then the total number W of possible methods of their arrangement is equal to [2]

$$W = \frac{\left(\frac{1}{4}\nu_1\right)!}{\nu_2!\left(\frac{1}{4}\nu_1 - \nu_2\right)!}. \qquad \text{(VII, 20)}$$

Here the numerator gives the total number of re-arrangements of C atoms and vacant sites, the first denominator factor refers to the transpositions only of carbon particles one replacing another, while the second denominator factor pertains solely to the rearrangements of vacant sites. All arrangements of the C atoms — as a first approximation — are assumed to be equally probable, which is valid for very dilute solutions.

For any given fixed arrangement the entropy amounts to

$$S = \nu_1 S_1 + \nu_2 S_2, \qquad \text{(VII, 21)}$$

where S_1 and S_2 are constants.

For the given composition with any arrangement of the C atoms we have

$$S = \nu_1 S_1 + \nu_2 S_2 + K \ln W. \qquad \text{(VII, 22)}$$

1) See foot-note on page 429.
2) This method of computation is, apparently, strictly valid only for the independently acting particles of ideal gas.

Whereupon

$$\bar{S}_2 = \frac{\partial S}{\partial \nu_2} = S_2 + K \ln \frac{\frac{1}{4}\nu_1 - \nu_2}{\nu_2} \qquad \text{(VII, 23)}$$

and

$$\mu_2 = \bar{H}_2 - T\bar{S}_2 = \bar{H}_2 - TS_2 - KT \ln \frac{\frac{1}{4}N_1 - N_2}{N_2}. \qquad \text{(VII, 24)}$$

Assuming further that

$$\mu_2 = \bar{H}_2 - TS_2 - KT \ln \frac{1}{4} \qquad \text{(VII, 25)}$$

and comparing the expressions (VII, 24) and (VII, 25), we find

$$\mu_2 = \mu_2^\circ + KT \ln a_2, \qquad \text{(VII, 26)}$$

$$a_2 = N_2 \gamma_2 = \frac{N_2}{N_1 - 4N_2}. \qquad \text{(VII, 27)}$$

Thus the variation of the activity coefficient of carbon with its concentration in gamma-iron may be described by formula[1]

$$\gamma_C = \frac{1}{1 - 5N_C}. \qquad \text{(VII, 28)}$$

This formula was checked by Temkin and Schwartzmann on the basis of experimental data for equilibria

$$\underline{C}_{(\gamma\,Fe)} + CO_2 = 2\,CO, \qquad \text{(VII, n)}$$

$$\underline{C}_{(\gamma\,Fe)} + 2\,H_2 = CH_4, \qquad \text{(VII, o)}$$

pertaining to solid solutions of C in γFe. It revealed that the values of

1) V. I. Arkharov called our attention to the following. In deducing the formula for γ_C, Temkin and Schwartzmann unjustifiably assume that the number of vacant sites for carbon amounts to $\frac{1}{4}$ of the number of iron atoms. In fact, if one considers the possibility of atom arrangement not only in the center of the given cube, but also in the centers of its edges, which, in turn, are centers of cubes, their number is considerably greater and is equal to the total number of iron atoms. If, in addition to this, one should take into account the possible arrangement of the C atoms at the points $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, then it will amount to the double number of iron atoms. Hence, the expression (VII, 28) should be considered as strictly empirical.

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$$K_1 = \frac{p^1_{CO}}{p_{CO}\, N_C\, \gamma_C}; \quad K_2 = \frac{p_{CH_4}}{p^1_{H_2}\, N_C\, \gamma_C} \qquad \text{(VII, 29)}$$

almost fail to change at all with the composition of the solid phase.

Yet, they greatly and regularly increase with N_C, assuming that the solid solution is ideal ($\gamma_C = 1$).

Moreover, formula (VII, 28) accords satisfactorily also with the experimental data pertaining to the activity of carbon dissolved in liquid iron (up to 3% C). The experimental values of a_C were obtained by two independent methods - according to the chemical equilibrium data and by means of E.M.F. measurement [16].

Samarin and Schwartzmann [17] explain the growth of γ_O with carbon concentration also without resorting to the assumption of the existence of CO molecules in liquid iron. The principal reason for the rise of γ_O is seen by them in the increase of the free volume of liquid during the solution of carbon. The latter deforms the lattice of iron and disturbs the coordination of Fe atoms in liquid metal. This leads to the growth of the number of the possible sites (consequently also of arrangements) for oxygen atoms[1], i.e., decreasing its activity coefficient.

Thus, in all probability, carbon monoxide, as other diatomic gases, does not dissolve in iron in the form of molecules.

It dissociates into C and O atoms, which form some kind of groups with the metal particles.

In conclusion let it be noted once again, that the study of the equilibria of gases (H_2, CO, H_2S, H_2O, O_2, N_2, SO_2, etc.) with iron and certain non-ferrous metals allows only a partial solution of the existence mode of dissolved elements. It becomes possible only to establish that they enter into structural complexes with metal in the form of individual atoms[2]. Whatever the nature of their bonds with their neighbors - covalent, heteropolar, or metallic - this method proves unfit to determine. It, therefore, remains unclear whether the element exists in the ionic or in

1) Which, however, probably form here replacement solution, and not those of intrusion.

2) In this case the crystalline lattice suffers deformation, the energy level of electrons in the metal lattice changes, "defects" appear which assure a greater mobility of the particles. For example, it is probably due to this fact that the energy of loosening falls rapidly with the growth of carbon concentration [70] from 69000 (pure Fe) to 34000 cal/mole (at 5% C) during the diffusion of iron atoms in carbon iron.

the atomic states, or whether it forms molecules of the Fe_xC type with metal.

2. FUSIBILITY DIAGRAMS

Attempt were made in a series of investigations to solve the problems of the molecular state of dissolved elements on the basis of a thermodynamic analysis of the fusibility diagram lines. This method, in particular, was used repeatedly in the studies of iron alloys with carbon and silicon.

The method is based on the assumption that major deviations from the system of the laws of perfect solutions are caused by the formation of molecules of chemical compounds either among the unlike atoms (negative deviations), or among like atoms (associations, positive deviations). For this reason such compositions and dissociation constants are being selected for chemical compounds as would permit bringing the equations for perfect solutions into accord with the experimental curves. The molecules of these compounds are then considered to represent the mode of existence of the dissolved elements.

However, this method is probably strictly applicable only for sufficiently rarefied gases. In condensed phases the presence of sharply expressed forces of interaction between the A and B (or A and A)[1] particles, which differ markedly from other atoms, frequently does not lead to the formation of molecules. Quite often, instead of the isolation of minor groups of atoms, this results in the ordering of the arrangement of a considerable number of them in space. Most clearly this is manifested in crystals and is valid both for the ionic bond (for instance, of NaCl), and for covalent linkage (for example, in SiC).

The foregoing makes the reviewed method ambiguous. Like the fusibility diagram itself, it indicates only that there exist some groups of particles. It does not permit one to judge, however, whether there are molecules, atoms, or ions in the mentioned phases, i.e., it is impossible fully to determine the character of bonding and the existence mode of the element dissolved in metal. Let us examine a few examples of such investigations.

BINARY SYSTEMS.

Akhumov [19], in a review of the preceding attempts to utilize Schroeder's equation for the analysis of fusibility diagrams, applied it to the liquidus lines for three systems: Al - Si, Fe - Si, and Fe - C.

To bring this equation into accord with the coordinates of the corresponding eutectic point he assumes that silicides and carbides of iron exist in the form of associated molecules $(Fe_3C)_n$ and $(FeSi)_m$.

1) In a number of cases the interaction of a particle with the whole crystal may, in the order of magnitude as a first approximation, be evaluated on the basis of interaction energy with the closest neighbors. However, there, of course, is an essential difference between these quantities.

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The best possible agreement with the experiment occurs when n = 2, and m = 6, i.e., when there are six atoms of iron contained in each polymer.

Chuyko, who was able to operate with more accurate values of the heats and points of melting of iron and its carbide, came to a similar conclusion. The theory concerning the existence of $(Fe_3C)_2$ molecules, in his opinion, enables the calculation of the eutectic melting point to be made with an error of merely some 3% (1460 instead of 1407°K).

If, on the other hand, one should proceed from the assumption of the existence in the melt of Fe_3C, or FeC, or C particles, then the error would increase appreciably (instead of 1407°K it would respectively be 1256; 1473 and 1520°K) and attain 11; 5 or 3%. A conclusion is drawn therefrom to the effect that the most probable forms of carbon existence in iron are constituted by $(Fe_3C)_2$ and FeC molecules and not by those of Fe_3C.

Gerassimov [20] and others [21] arrive at opposite conclusions, namely that carbon in these solutions is to be found primarily in the form of Fe_3C.

The first determines the activities of Fe and C, as well as those of Fe_3C and Fe at 800-1000°C, by making use of the equilibrium data of austenite with CO_2 and CO. On the basis of the activity versus concentration form of relationship he deduces that austenite may be regarded as a regular solution of a "singular modification" of Fe_3C in Gamma-iron.

It should be noted here, that the author himself observes the presence of a systematic error in the experimental data of other authors [22], which he had actually used in his calculations[1].

Some investigators [21] in their computations utilize the known thermodynamic equation

$$d \ln \frac{x}{x'} = -\frac{Q}{RT^2} dT , \qquad \text{(VII, 30)}$$

pertaining to the equilibrium of two perfect solutions of different phase states.

In duscussing the shape of the curve GS (equilibrium of carbon solutions in Gamma- and Alpha-iron) they assume x' = 100 and modify equation (VII, 30) to take the aspect of

$$\lg x = -\int_{T}^{T_{melt}} \frac{Q}{4{,}575\, T^2} dT + 2. \qquad \text{(VII, 31)}$$

1) For more precise data consult [23].

Here x stands for the contents of iron in the Gamma-phase, mol. %;
Q is the heat of transformation;
T_{melt} is the melting point.

The value of the integral is determined by them from the graph plotted according to the coordinates: heat content - temperature. The area taken thereby is limited with respect to the X-axis by the temperatures of the given T and 906°C while with respect to the Y-axis it is bound by the heat contents curves for pure iron and the extrapolated (in the region of lower temperatures) branch for Gamma-iron. In brief, the integral for Alpha-Gamma solutions is approximatively replaced by them by that pertaining to the transition of Alpha-iron into Gamma-iron.

Then, on the basis of the known right part of equation (VII, 31) the value of x is being determined. It appears to correspond somewhat better to the experimental composition, if carbon is assumed to be found in austenite in the form of Fe_3C molecules and not as free atoms.

In passing over to the equilibrium of the melt with austenite, they integrate equation (VII, 30), assuming Q = 3760 cal/g-atom Fe and presuming that Q does not change with temperature and composition.

Then

$$\lg \frac{x}{x'} = \frac{3760}{4{,}575}\left(\frac{1}{T} - \frac{1}{1791}\right) = \frac{822{,}6}{T} - 0{,}4593 . \qquad \text{(VII, 32)}$$

The comparison of equation (VII, 32) with the experimental curves is effected by them in three different ways with the following allowances:

a) carbon is present in the melt and in austenite only in the form of Fe_3C molecules;

b) atomic carbon is to be found in the solid solution, and carbide in the liquid solution;

c) in both phases only C atoms are present.

It appears that versions a and b differ little one from another, and are closer to the observed data than version c. Whence a deduction is made to the effect that carbon is present in the melt predominantly in the form of Fe_3C, with the latter being to a certain degree dissociated into C and Fe. As to the mode of carbon existence in austenite in the conditions approaching the IE line, they hesitate to formulate any definite conclusion.

Analogous ideas on the existence in melts of Fe_3C molecules partially dissociated into atoms have also arisen more recently [24]. In this case the calculations deal with carbon saturated liquid solutions, and are based on the applicability of the mass action law in its ideal form.

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Here, expressions for the equilibrium constants of the following four interactions are being recorded for iron-carbon melts:

$$C_{(graph)} = \underline{C}, \qquad \text{(VII, p)}$$

$$C_{(graph)} + 3\underline{Fe} = \underline{Fe_3C}. \qquad \text{(VII, q)}$$

$$\underline{C} + CO_2 = 2CO, \qquad \text{(VII, r)}$$

$$\underline{Fe_3C} + CO_2 = 3\underline{Fe} + 2CO. \qquad \text{(VII, s)}$$

Making use, then, of the experimental data on carbon solubility (from 4.24%C at 1150°C to 9.71% at 2500°C) and the values of the equilibrium constants for the reactions (VII, q) and (VII, r), one obtains

$$\lg K_p = -\frac{3890}{T} + 0{,}929 \qquad \text{(VII, 33)}$$

and

$$\lg K_q = -\frac{1710}{T} + 1{,}234. \qquad \text{(VII, 34)}$$

Whereupon the "composition" of the carbon saturated Fe - C solution is calculated.

Thus at 1150°C temperature the mole fraction of Fe_3C amounts to 0.318, while for free carbon it comprises only 0.016. The converse appears to be true at 2500°C, when the first is equal to 0.266, whereas the second attains 0.333. In other words, at relatively low temperatures the greater part of C is combined into Fe_3C molecules and it is only at high temperatures that one should reckon with considerable concentrations of atomic carbon.

It is further stated /247 that the assumption of the existence in the melt of other molecular forms, namely FeC and Fe_2C, precludes the possibility of an agreement between the calculation results and the data on solubility. It is maintained that this fact constitutes the main proof that the calculated composition of the melt actually corresponds to reality.

Yet, it seems highly improbable, that with an appropriate choice of the temperature dependence of the dissociation constant, one should still fail to produce agreement with the observed data upon selection of other molecular forms.

The foregoing illustrates once again the ambiguity of the adopted method.

TERNARY SYSTEMS.

A similar method /247 is also applied for the calculation of the molecular composition of the three-component carbon saturated melt Fe - Si - C. In addition to the afore-cited interactions account is also taken of the reaction

$$n\underline{Fe} + \underline{Si} = \underline{Fe_nSi}. \qquad \text{(VII, t)}$$

A simultaneous solution of the equations for equilibrium constants permits to compute the solubility of C, if the values of n and K_t are known. In varying n from 0 to 3 and upon selection of the value of K_t, one finds the accord with the experimental data to be most satisfactorily achieved when n = 3 with K_t changing with temperature as per equation

$$\lg K_t = -\frac{3150}{T} + 3{,}45. \qquad \text{(VII, 35)}$$

On the basis of this a conclusion is drawn that silicon is present in the melt in the form of Fe_3Si molecules which are partially dissociated into atoms.

The obtained result, like the preceding ones, is only in formal agreement with the experimental data. However, in this concrete instance the shortcomings of the method under consideration manifest themselves in a particularly graphic manner.

The obtained /247 temperature dependence K_t conflicts with the direct thermodynamic measurements. According to the latter, the solution of silicon in iron is accompanied by a powerful release of heat ($\Delta H_{1600°C} \cong$ - 29000 cal/g atom Si).

Yet, from equation (VII, 35) it follows that the reaction between Fe and Si in condensed state occurs with an absorption of heat, i.e., the postulated compound disintegrates with falling temperature and becomes more stable with its rise. Furthermore, not only the temperature dependence, but even the selected composition of the compound (Fe_3Si), clearly fails to conform to reality.

Results, produced by means of a number of independent methods, suggest that silicon is present in liquid iron mainly in the form of groups (possibly molecules) of a different composition, namely that of FeSi.

Thus, the results of measurement of the electromotive force /257 arising in a concentration chain

$$\begin{matrix}\text{Fe, Si, C}\\(43\%\ \text{Si})\end{matrix} \Big| \ CaO,\ MgO,\ SiO_2 \ \Big| \ \begin{matrix}\text{Fe, Si, C}\\(x\ \%\ \text{Si})\end{matrix}$$

at the temperature of 1470°C, show that the curve of its dependence upon composition has a sharp deflection (fig. 156) at 32.5% Si (49 atom. %).

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As is well known, such curves are characteristic for potentiometric titration, when weakly dissociated low-solubility chemical compounds are being formed.

In this case the break indicates the existence in the melt of a sufficiently stable iron silicide of FeSi composition.

Furthermore, analysis of surface tension in Fe - Si systems revealed /26/ that it drops with the increase of silicon contents along a curve which also has a break round 34% Si.

A similar relationship was also established /27/ for the interphase tension at the boundary Fe,Si - slag (fig. 157).

These data confirm, through a different independent method, the existence in the melt of the FeSi compound. Moreover, they emphasize the homeopolar character of atomic bonds in it.

Indeed, since the solution of silicon in iron is accompanied by considerable liberation of heat, the interaction between Fe and Si must be more powerful than between like particles. In view of this fact the silicon atoms cannot be expelled onto the surface of the melt, and the decrease of the surface and interphase tensions (in low silicon melts) is to be attributed to the capillary activity of the FeSi molecules. The latter becomes possible if the bonds in them have a covalent character (see also /28/).

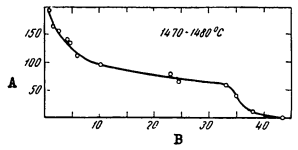

Fig. 156. Effect of silicon contents in high-temperature galvanic element Fe, C, 43% Si (slag) Fe,C, x% Si per e.m.f.

Legend: A) E.M.F., mV
B) Si contents, %.

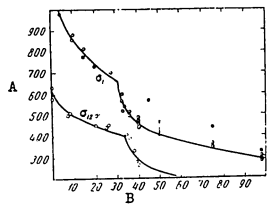

Fig. 157. Isotherms of surface (σ_1) and interphase (σ_{12}) tensions for iron-silicon alloys at the boundary with hydrogen and slag (1480°C).

Legend: A) Tension erg/cm^2
B) Si. contents, %

Finally, the third independent method /29/ is based on the determination of the heats of mixing of silicon and iron both at room temperature and at 1600°C. The maximum heat of mixing is known /29/ in both cases to correspond to 50 atom.% Si. Such character of the plot also lends credence to the theory that FeSi constitutes the stable compound in the melt.

The differential heat of silicon solution in iron determined from these data turned out to be equal[1] to 28500 cal, while the activity coefficient of Si amounted to 0,0007[2]. These results illustrate once again the stability of the FeSi chemical compound in the melt, which is also consonant with the character of the maximum revealed by the liquidus curve.

This circumstance is also corroborated by Yelyutin and Levin /31/, who evaluated the equilibrium constant of interaction

$$Fe_{(liq)} + Si_{(liq)} = FeSi_{(liq)}$$

in the assumption that

$$\Delta F^{\circ}_{1873\ K} \sim \Delta H_{1873\ K} = -29\,000 \text{ cal.}$$

1) More recent measurements /30/ showed 29000 cal per 1 g/atom of silicon.
2) A close value of the activity coefficient (0.0005) was calculated in the work by Geld and Kuznetzova.

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Hence,

$$\lg K_{1873} = -\frac{\Delta F^\circ}{4{,}575\,T} \approx 3{,}4$$

or

$$K = 2{,}5 \cdot 10^3.$$

The high value of the constant point, to the practically total undissociation of ferro-silicide at 1600°C.

In conclusion let it be said that a certain indication as to the stability of the FeSi complexes is to be found in the surveys of the equilibrium of gaseous hydrogen with liquid iron-silicon alloys. For example, according to the available data [32] all isotherms of hydrogen solubility at atmospheric pressure over the temperature range 1350-1650°C show a clearly defined minimum corresponding to 50 atom. % Si.

Summing up the aforesaid, it may be well to emphasize again the fact, that the processing of the data pertaining only to equilibria (fusibility diagrams, equilibrium constants, solubilities, etc.) cannot provide an unambiguous answer to the question concerning the mode of existence of an element dissolved in metal. Moreover, underestimation of the results obtained by other independent methods of experimental investigation is apt to lead sometimes to absolutely wrong conclusions.

3. DIFFUSION OF GASES IN METALS

The fundamental regularities of the diffusion of gases through metals are closely connected with their solubility. Indeed, in a number of cases it becomes possible — during the analysis of gas diffusion through metallic membranes — to consider their boundary surface as being in a state of equilibrium with gas. By virtue thereof the concentration gradient c_1-c_2 in the equation of the diffusion flow may be expressed through partial gas pressures p_1-p_2 on both sides of the membrane.

$$q = -DS\frac{dc}{dx}\tau \sim -DS\frac{c_1-c_2}{x}\tau = -\frac{DSk}{x}(\sqrt{p_1}-\sqrt{p_2})\tau, \qquad \text{(VII, 36)}$$

where D - diffusion coefficient;
S - surface of the membrane;
x - thickness of the membrane;
τ - time

Considering the diffusion in the conditions when $p_2 = 0$, we have

$$q = -\frac{DSk}{x}\sqrt{p}\,\tau, \qquad \text{(VII, 37)}$$

i.e., the rate of diffusion must be proportional to $\sqrt{p}$, if the molecules of the diatomic gas dissociate into atoms in the process of dissolution.

Thus, in studying the effect of pressure upon the diffusion rate of gas in metal, it becomes possible to elucidate the character of the transformations occurring with the molecules of gas in the process of their solution. Experiments, in the main, support this fact.

Perminov [33], for instance, found the diffusion rate of hydrogen through iron to be proportional to $\sqrt{p_{H_2}}$ at temperatures ranging from 320-550°C and pressures up to 350 atm.

Similar regularities were found to be valid also for a series of other metals (see, e.g., [11], [34]). It should be noted, however, that equation (VII, 37) is strictly conformed to only when the pressures are sufficiently high. In the region of low pressures, deviations are to be registered which are related to the commensurability of the adsorption and diffusion rates. This fact determines the impracticability of the initial position, since the metal surface does not happen to be saturated with gas [35].

Similar correlations are also observed during electrolysis. In this case hydrogen, which discharges at the cathode, partially molizes and passes then into the gaseous phase, and partially dissolves in metal diffusing through it.

A substantial supersaturation of metal with hydrogen in relation to the gaseous phase may be achieved thereby, since the concentration of atomic hydrogen at the cathode surface exceeds considerably the concentration which is at equilibrium with gas. For instance, according to Nossyreva's data [36] it is possible to supersaturate iron with hydrogen substantially by means of electrolysis, in increasing the contents of hydrogen from 50 to 90 $cm^3/100$ g. In consequence of this, very considerable pressures, attaining tens and hundreds of atmospheres [37], may be produced in hollow cathodes during electrolysis.

It turns out [38] that the diffusion rate of hydrogen in the cathode at sufficiently high current densities I is proportional to $\sqrt{I}$. More precise [35] is equation

$$D = k\Theta\sqrt{I}, \qquad \text{(VII, 38)}$$

in which $\Theta = \varphi(I)$ is a coefficient tending to unity with the growth of I and which reflects the deviation from the linear relationship of D versus $\sqrt{I}$ when the cathode-current densities are small. In other words, the fact is taken into account that the diffusion rates of hydrogen and its discharge at the cathode become comensurable when the I is small.

The validity of equation (VII, 38) is directly related to the fact that the concentration of hydrogen at the cathode surface is proportional to the intensity of the current. In this case it is not difficult to produce equation (VII, 38) from equation (VII, 37). Whereupon a deduction suggests

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itself to the effect that the diffusion of hydrogen through metal, in the case of electrolysis, also occurs in the atomic form. This is corroborated by the fact that the activation energy of the hydrogen diffusion process proves to be the same both in the case of the passage of current (electrolysis) and in its absence (hydrogen from the gaseous phase).

For example, according to certain data [39], the rate of hydrogen diffusion through metal can be described by equation

$$D = k_0 e^{-\frac{4550}{T}} \cdot \Theta \cdot I, \qquad \text{(VII, 39)}$$

from which it follows that

$$E \cong 9100 \text{ cal/g-atom.}$$

The obtained value practically coincides with that of the activation energy of the process of hydrogen diffusion through iron, which, according to the same data, is equal to 9530 cal/g-atom, and confirms the existence of a single mechanism of diffusion both for electrolytic and gaseous hydrogen.

4. ELECTROLYTIC EFFECT IN METAL ALLOYS

Interesting material for the evaluation of the mode of existence of elements in dissolved metal is made available by investigations into the influence of the electric field. It appears that the passage of direct current through solid and liquid metal alloys is accompanied by transfer of matter. Moreover, the migration rate of the particles of various components is not the same, which causes a non-uniform concentration distribution in the sample along the direction of the field.

The first attempts to subject metal alloys to electrolysis by passing the current through abutting copper and aluminum cylinders resulted in a failure, in spite of the long duration of these experiments (10 years). It appeared impossible to trace the passage of the substance from one cylinder into another.

Further investigations, a review of which is provided, for instance, by Romadin and other authors [40], [41], exposed the reasons for this and other failures. They consisted in the fact that the experiments were conducted with low-density currents and at low (room) temperatures.

Upon selection of appropriate conditions, a noticeable mass transfer may be registered both in solid and liquid metals. In particular, during the passage of direct current through an incandescent tungsten wire its cross section decreases at the positive pole and increases at the negative pole. This does not occur in the case of alternating current.

This probably explains the shorter life of incandescent lamps which operate with direct current and their burning out in the vicinity of the positive pole.

Such "self-transfer" of metal points to the participation in the electric current not only of conduction electrons but also of ions. It is true that the part of the latter in the transfer of electricity is small.

The electrolytic effect is most readily revealed in alloys and not in pure metals. Owing to the difference in the mobility of ions there arise concentration changes in the former. The composition of the alloy happens to be different at the positive and negative poles.

The number of binary alloys studied from this point of view is large enough. Some of the results obtained are recorded hereby, namely, the directions of the displacement of some or other elements. Under the influence of direct current the following components of binary alloys are being transferred over to the cathode:

Alloy:	Au-Pb	Au-Cu	Au-Pd	H-Pd	Fe-C	Fe-B	Fe-N
Transferred are:	Pb	Cu	Pd	H	C	B	N[1]

The effect of electrolytic transfer is greater in liquid alloys than in solid alloys, due to the greater mobility of the particles.

The influence of direct current was investigated for a great variety of liquid alloys - low-melting amalgams, non-ferrous and light metals, and certain iron alloys (of the Fe-P and Fe-S systems) at temperatures up to 1600°C.

In a number of cases the electrolysis of alloys in capillaries was accompanied, according to Kreman, by very considerable concentration changes. Thus, for instance, for the alloy of bismuth with zinc, a considerable accumulation of zinc was registered at the cathode. The concentration gradient between the anode and the cathode increased quite strongly with growing current density and attained 75% at 8-10 amp/mm^2. Yet, in the Fe-P and Fe-S melts no effect was observed.

It should be noted, however, that these data are not sufficiently accurate and not too reliable. This was first noticed by Grebenshchikov [44]. In checking, together with Tarassov, the effect of direct current on liquid low-melting metal alloys, he studied their composition in various sections of a connective capillary by method of electrical conductivity without freezing of the system (i.e., before crystallization). It was revealed thereby that the observed effects were considerably lower than those recorded by Kreman. Romadin and Schwartz arrived at similar conclusions later on.

To illustrate the foregoing table 20 provides a comparison of the results of Kreman's and Romadin's measurements for a few non-ferrous alloys.

1) According to Prosvirnin's data [42] nitrogen is transferred to the cathode, according to other data [43] - to the anode.

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Table 20. Comparison of Electrolytic effects.

Alloy	Effect, %		Transferred to the cathode
	According to Kreman	According to Romadin	
Pb—Cd	30	1,2—2,6	Cd
Sn—Cd	6	0,5—2,5	Cd
Pb—Bi	42	6,5	Pb
Sn—Bi	40	5,5	Sn
Cd—Bi	65	4,5	Cd
Ag—Pb	8	1,0	Ag
Cu—Sn	20	3,3	Cu

Although Kreman's data are clearly over-rated, the direction of the displacement of components as established by him is confirmed by Romadin's experimental data. This allows one to believe that the series proposed by Kreman: anode - Bi, Sb, Hg, Pb, Sn, Zn, Cd, Cu, Ag, Al, Na, K - cathode, which in a certain measure is analogous to the series of the ionization potentials of elements, does not deviate very much from reality.

TRANSFER OF CARBON IONS

In discussing the magnetic properties of the intermetallic compounds of the elements of transition groups (Fe_2, B, Fe_3C, Fe_4N, and Fe_2N), Dorfmann and Kikoin [45] proposed diagram of their structure, according to which all components figure in this alloy in the form of positive monovalent ions Fe^+, B^+, C^+, N^+. In other words, the authors assume that "on the average one electron from each of the participating atoms will separate into the 'general cauldron' of metal". Lebedev [46] came simultaneously to a similar conclusion concerning the state of carbon in cementite.

On the basis of the sizes of tetrahedral interstices and C atoms, as well as the great mobility of the latter, he reached the following general conclusion: "it is fully justifiable to believe that a positively ionized carbon atom .... surrenders its electrons into the general cauldron". Subsequent experiments, carried out by a number of investigators and confined to the study of the effect of direct current on Fe- C alloys, have confirmed this theory.

Thus, Romadin [40] subjected a steel wire, 0.6 mm in diameter and 16 mm long, to electrolysis. It was welded onto platinum electrodes soldered into an evacuated flask. The initial metal contained 0.64% C, 0.72% Mn, 0.17% Si, 0.024% P, and 0.017% S. The voltage at the electrodes varied from 0.7 to 1.7 v, and the current from 7.4 to 9.4 amp, which corresponds to a current density of 26.1 - 33.2 amp/mm^2. The temperature of the wire attained 940 - 1010°C.

The experiment lasted from 10 to 100 hours. Thereupon the wire was subjected to metallographic analysis. In all fifteen tests transfer of carbon towards the cathode was registered.

The initial wire had a uniform structure and consisted of evenly distributed grains of sorbite-like pearlite and a ferrite network.

The passage of direct current sharply changed its structure. In the regions adjacent to the cathode practically nothing but pearlite was to be found, whereas the anode layer consisted almost entirely of pure ferrite.

In addition to this, during the particularly long tests (100 hours), a marked penetration of carbon from the steel wire into the platinum cathode was observed. In consequence of this, the latter became hard and brittle, whereas the platinum anode, on the contrary, preserved its original softness.

As one should have expected, no change in the wire structure was observed during the experiments with alternating current, i.e., no transfer of carbon towards the cathode was to be registered.

Similar results were obtained by Prosvirnin [42] and Guterman [47]. Photomicrographies of the regions of the steel wire adjacent to the electrodes (0.5% C) taken after the "electrolysis" are recorded in fig. 158 and illustrate the aforesaid.

A number of investigators [43], [49] carried out their experiments in a somewhat different way. One or several sections (each up to 10 min. long) of a pure iron wire were carbonized. The other separating sections were protected from cementation, for example, by prior copper plating. The ends of the carbonized sections were marked off and the current with a density of about 30 amp/mm^2 was passed through the wire enclosed in vacuum at a temperature of 1000°C for a period from 8 to 25 hours.

The subsequent metallographic investigation,[1] conducted on both sides of the carbonized section, showed that in the case of alternating current treatment a steady diffusion of carbon was to be observed in the direction from the spot subjected to cementation towards pure iron.

On the other hand, during the passage of direct current diffusion towards the cathode turned out to be considerably more intensive than in the direction of the anode. The distribution of carbon concentration in relation to the carbonized section becomes asymmetric (fig. 159). The diffusion flow to the cathode exceeds that for the direct current, the converse appears to be true in the case of the flow directed towards the anode. Consequently direct current accelerates the movement of carbon towards the cathode and retards its displacement towards the anode.

The results produced prove that carbon, dissolved in iron, is present in the form of positive ions like the atoms of metal (which are, apparently, less mobile). Moreover, they permit estimation of the magnitude of the "electrolytic" flow and the transfer number of the carbon ion. The latter permits a conclusion to be made concerning the size of its charge.

1) Sometimes accompanied by measurement of the specific resistance.

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Fig. 158. Photomicrography of the steel wire sections adjacent to the anode (a) and cathode (b) after the passage through it of direct current.

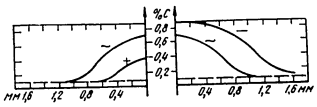

Fig. 159. Distribution of carbon along the wire after the passage of direct (+, −) and alternating (~) current.

CHARGE OF THE CARBON CATION

The transfer numbers of carbon n, calculated from the cited experimental data, are small; they are of the order of $10^{-7} - 10^{-6}$. The temperature dependence of n is analogous to that for the coefficient D of carbon diffusion in iron. Indeed, as may be seen from fig. 160 the curves n(T) and D(T) are almost parallel. In view of this, one can assume that during normal diffusion the particles of carbon carry a positive charge. Then the activation energies of both processes will be approaching each other, which fact explains the mutual parallelism of the n(T) and D(T) plots.

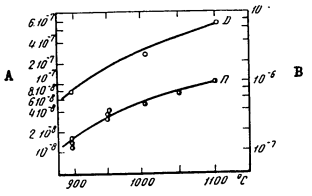

Fig. 160. Effect of temperature on the transfer number and the coefficient of diffusion of carbon in iron.

Legend: A): Diffusion coefficient, cm^2/sec.
B): Transfer number, n.

At the present time the following two equations were advanced [40], [45] for n:

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$$n = \frac{96\,500\, eNc_2 d}{300\, RT\varkappa}(D_2 z_2 - D_1 z_1)\,, \qquad \text{(VII, 40)}$$

$$n = \frac{96\,500\, eNc_2 D_2}{300\, RT\varkappa}\left(z_2 - z_1 \frac{V_2}{V_1}\right). \qquad \text{(VII, 41)}$$

In them c_2 strands for the concentration of the dissolved element;

D_i and z_i are the coefficient of diffusion and the charge of ion;

V_i is the atomic volume;

$\varkappa$ - specific conductivity.

Experimental control of these expressions with amalgams of Li, Na, K, and Cs [45] shows that equation (VII, 41) is more accurate, and is, therefore, usually given preference. Lebedev and Guterman [49] have made an effort to apply this formula to determine the charge of the carbon ion on the basis of the experimental value of its transfer number.

The calculation is complicated essentially by the indefiniteness of the iron ion charge which is included in expressions (VII, 40) and (VII, 41). They, just as the ions of other metals, may have different charges in the alloy and in the pure substance. Moreover, magnetic measurements indicate that differently charged ions are simultaneously present in metal. Thus, for instance, it is assumed [50], [51], that metal atoms in solid solutions have the following charges:

$$Cr^{2+},\ \underline{Cr^{\circ}},\ Mn^{3+},\ \underline{Mn^{+}},\ Fe^{+-},\ \underline{Fe^{2+}},\ Co^{6+},\ Co^{3+},\ \underline{Co^{2+}},$$
$$\underline{Pd^{\circ}},\ \underline{Pt^{\circ}},\ \underline{Ni^{\circ}}$$

(underlined is the most probable state).

In view of this indeterminacy, Lebedev and Guterman made a few assumptions concerning the ion charges in their calculations. It transpired, that with $z_2 = 1$ (i.e., in the presence of C^{+}) the observed values diverge sharply from those calculated as per both equations. When $z_2 = 2$ (i.e., in the presence of C^{2+}) the experimental data shows satisfactory agreement only with equation (VII, 40). As regards the more precise formula (VII, 41), it comes into accord with the results of the experiment either when $z_2 = 3$ (i.e., C^{3+}), or when $z_2 = 4$ (C^{4+}), if z_1 is equal, respectively, to 1 (i.e., Fe^{+}) or 2 - 3 (Fe^{2+}, Fe^{3+}).

Since Fe^{2+} seems to be the most probable form for iron ions, they are inclined to admit that an ion of carbon carries from 3 to 4 charges.

The fact is that $z_2 > 1$ follows also from the following computations [48]. The mobility of the B ions, determined experimentally for carbon, amounts to 1.6 - 2.2 · 10^{-5}cm/sec v. at 1350° K. If it be evaluated from

the equation

$$B = \frac{z_2 FD}{RT}\,,$$

in which D = diffusion coefficient of carbon, while F = 96 500 coulombs, then it should total 0.825 · 10^{-5} cm/sec v. for $z_2 = 1$. In other words, in order to reconcile the calculated values of B with the experimental data it is necessary to assume $z_2 > 1$ and equal to 2 or 3.

Of course, the recorded evaluation methods of the magnitude of z_2 bear a very approximative character. There is no doubt, however, that carbon dissolved in iron remains in the form of cations possessing more than one charge[1].

TRANSFER OF HYDROGEN IONS

For the identification of the nature of the intrusion phases, which form during the solution of H, C, N in iron, of great importance is the study of the properties of the hydrogen-saturated transition elements (for example, Pd).

As shown by theoretical calculations, ordinary hydrogen, the atoms of which are co-valently bound into H_2 molecules, changes into "metallic" hydrogen under very high pressures. In other words, the valence electrons of its atoms become common not for two, but for a large assemblage of nuclei. Both forms can co-exist at pressures of the order of 250,000 atm[2].

Such pressures, so far, have not been realized. However, the metallic properties of H may come into display in its solutions with metals, as a result of a peculiar internal pressure caused by the intrusion of hydrogen into the lattice.

Indeed, if one takes into account the compressibility factor of palladium (0.4 · 10^{-6} cm^2/kg) and the expansion of its volume upon saturation with hydrogen (~11%), then the "internal pressure" produced could be estimated at 270,000 atm [53].

In these conditions, hydrogen should behave like metal, as, in fact, has been confirmed by experiments.

As a matter of fact, experiments show that in this case direct current provokes quite an intensive migration of hydrogen towards the cathode [54]. This was ascertained by a variety of methods, including measurements of resistivity, of the electromotive force, and so on.

1) In view of this, the average charge of all carbon cations must not necessarily be integral.

2) Incidentally, according to other data [52], this pressure is even greater and comprises at least 400,000 atm.

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The mobility of hydrogen ions in Pd grows rapidly with temperature and greatly (by hundreds of times) exceeds that for carbon in iron. Its high values in the electric field are in full accord with the very small sizes of the hydrogen cations, i.e., protons[1].

In this connection, it is well to note also the exceptionally high coefficient of hydrogen diffusion D (cm^2/sec) in metals. Its magnitude cannot be explained, unless one assumes that hydrogen is present in the ionic, and not in the atomic state.

According to Смуко, the coefficient of hydrogen diffusion D in Gamma-iron can be calculated at various temperatures with the aid of equation

$$\lg D = -\frac{2518}{T} - 1{,}9363 . \qquad \text{(VII, 42)}$$

Table 21 provides a comparative listing of the coefficients of diffusion in Gamma-iron for hydrogen, carbon, nitrogen, oxygen, silicon, and sulfur [54].

Table 21. Diffusion Coefficients of certain elements dissolved in Iron.

Element	Diffusion Coefficient, 10^5 $cm^2/24$ hours, at temperature, °C	
	1000	1100
H	106 000	149 000
C	1730—2330	3900—10 000
N	1170	3400
O	6.5	—
Si	—	100
S	—	8.5

The small activation energy of the process of hydrogen diffusion in iron is noteworthy. Thus, for diffusion in Alpha-iron it totals only 3750 cal/g-atom, while in Gamma-iron it is 11500 cal/g-atom, while, for example, for carbon in Gamma-iron it equals 32000 - 33000 cal/g-atom. [57]

This circumstance points to the negligible energy obstacles encountered by hydrogen during its migration from one interstice into another, i.e., emphasizing thus the very small sizes of its particles ("protons").

1) It should be noted here that a positively charged hydrogen particle present in the metal could only conditionally be termed as proton. Its properties are not identical to those of a "free" proton, since it remains in interaction with the whole crystal. Yet, it differs just as substantially from the atom of hydrogen, because of the surrender of the valence electron into the general cauldron.

Finally, Баумаков and Yevlannikov [58], on the basis of X-ray diffraction and electrochemical analyses of nickel containing hydrogen, came to the conclusion that the latter may be present in the metal in two forms.

They believe that in the process of electrolytic deposition of nickel, one part of the protons is adsorbed by the surface of nickel crystals, neutralized by electrons, and forms atoms which dissolve partially in metal or combine into molecules. The other part of the protons enters into the crystalline lattice together with the ions of nickel and forms a solid intrusion solution.

According to their data, the formation of a solid solution leads to the distortion of the crystalline lattice of nickel and to the growth of its parameter from a = 3.490 to a = 3.500 Å[1]. Upon annealing in vacuo the metal acquires normal parameters. Subsequent saturation with hydrogen (lasting cathodic polarization) leads to the intrusion of atomic hydrogen[2] which does not affect the lattice parameters.

5. SUSCEPTIBILITY AND SPLITTING OF THE X-RAY SPECTRA LINES OF METALS IN WHICH HYDROGEN WAS DISSOLVED.

SUSCEPTIBILITY

Palladium is known to be paramagnetic. This indicates that on the average there exists a certain effective number of unpaired electron spins in the d-shell in all atoms. A similar condition prevails also in the atoms of the other transition elements. The addition to them of other metals with filled d-shells (Ag, Au, Cu) causes the migration of the valence electrons, which previously belonged to them, on to the 4d level.

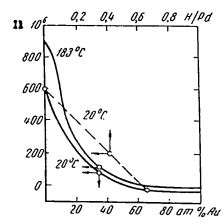

Fig. 161. Influence of the concentrations of hydrogen and gold upon the paramagnetism of their alloys with palladium.

1) Such extent of deformation resulting from hydrogen intrusion is unusually high and requires checking.

2) Which, according to the authors, is more rapidly adsorbed on the developed surface of the nickel crystals.

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As a result of this, the number of unpaired electrons diminishes and paramagnetism is consequently reduced. Such is the situation which arises, for instance, upon the addition of Cu, Zn, Al and other elements to nickel.

The number of unpaired electron spins in a gram-atom of palladium is equal to 0.55 N (where N is Avogadro's number). In other words, not every Pd atom has an unpaired electron in the 4 d band, since a proportion of electrons passes from the 5S level to 4 d. In view of the above, palladium's paramagnetism vanishes for instance, in alloys with gold when the percentage of the latter amounts to 55 atom %. As it may be seen from fig. 161, hydrogen, dissolved in Pd, produces such an effect.

With increasing hydrogen contents, paramagnetism of palladium drops almost linearly and disappears when the ratio of H to Pd equals 0.5 - 0.65.

The liquidation of paramagnetism of palladium with the help of Ag is achieved upon the introduction of 70% of silver. It is interesting to note that with increasing Ag percentage the solubility of hydrogen in Pd-Ag alloys decreases rapidly and reaches the zero point at about 65-70% Ag.

The recorded data also underline the metallic character of hydrogen dissolved in palladium, namely, the ionization of H and the transition of its valence electrons into the vacant 4 d-levels of Pd. This, in particular, explains the high solubility of H in Pd its decrease upon addition of Ag, which reduces the number of unpaired spins in the d-band.

SPLITTING OF THE LINES OF THE X-RAY SPECTRUM.

Krassnikov [59] studied the condition of hydrogen in metals by means of a method elaborated by him for the measurement of the distance $\Delta\lambda$ between the lines of the K_{α_1,α_2} doublet in the x-ray spectrum. According to his data, the stated distance for a number of metals (Cr, Mn, Fe, Co, Ni, Cu, Zn) decreases more or less smoothly with the increase of the atomic number (fig. 162).

Along with this, a hyperfine structure (splitting of the doublet in two) appears in the spectra [60]. It further transpires that $\Delta\lambda$ diminishes during dissolution in the hydrogen specimen and grows after the replacement of pure metal by its oxide (see the dotted curves in fig. 162). For each metal the variation of $\Delta\lambda$ comprises about 3.5%, while the width of the lines varies from 25 - 30%.

In this connection Krassnikov [61] observes the inadequacy of the accepted concepts, according to which the magnitude of the doublet difference is determined only by the atomic number and the structure of the electron shell. He believes that the variation of $\Delta\lambda$ under the influence of hydrogen points out to the intrusion of protons into the atomic electron shells[1]. Only this, he feels, can explain the effect of

1) One should rather assume that the ionized hydrogen atoms are located in the interstitial spaces (as well as the particles of C, N, etc.) and change the energy level of the electrons in the lattice of metal.

dissolved H upon the x-ray spectra which are governed by the behavior of the electrons closest to the nucleus.

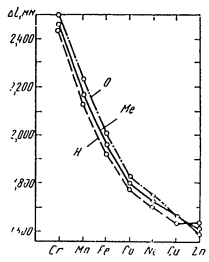

Fig. 162. Distances apart between the lines of the doublet K_{α_1,α_2} for a number of elements:

Me - pure metals; H - metals saturated with hydrogen; O - metal oxides.

According to the data (see fig. 162), the drop of $\Delta\lambda$, caused by hydrogen, is equivalent to the increase of the atomic number Z or the atomic weight A of the element. And conversely, the growth of $\Delta\lambda$ after introduction of oxide is equivalent to the decrease of A and Z.

Inasmuch as the observed drop of $\Delta\lambda$ is small and comprises only 10-20% of the effect produced by the increment of the atomic weight per unity, Krassikov assumes that there is a small and short-term growth of A at the expense of the statical and continuous redistribution of protons within the interior regions of the various atoms. This distribution of the protons in metal he terms as "proton gas" [62]. The latter constitutes "the protons of the given substance, since it is difficult to call them protons of ordinary hydrogen, or protons which present the fixed part of all atoms". Both the atomic bonds and the condition of the electron gas in metal are determined by the condition of the proton gas.

In this manner, Krassnikov comes to the conclusion not only to the effect that hydrogen, dissolved in a number of metals, remains in the form of protons, but that there exists a fairly deep and close bonding between them and the remaining atoms.

Later on Galaktionova [63] succeeded in accomplishing a series of x-ray diffraction studies of iron samples outgassed at high temperatures in vacuo and of specimens especially saturated with hydrogen. She was unable to reveal any difference in their structure, which fact repudiates the theory concerning the existence of hydrides in metal.

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Moreover, within the limits of precision of her measurements (± 0.0015 Å) the parameter of the Alpha-iron lattice remained unchanged. On the basis of this fact, she rejects the possibility of an intrusion of hydrogen atoms into the interstitial spaces, and believes that the entire quantity of hydrogen is present in the form of protons.

It should be mentioned, however, that according to the data of a number of other authors /64/ the intrusion of hydrogen into the interstitial spaces of iron causes a deformation of the lattice to the extent of 0.0005 A (with the contents of hydrogen amounting to 30 cm^3/100 g).

6. INTRUSION PHASES OF THE METALS OF TRANSITION GROUPS.

The above data refer to the ionized state of hydrogen dissolved in transition elements. It forms with them the phases of intrusion which were examined in detail by numerous investigators /65/, /66/. In them the metalloid particles M are arranged in the interstices of the metal (Me). Such distribution of M without substantial disruptions of the arrangement of the Me atoms becomes possible when $\frac{r_M}{r_{Me}} < 0.59$.

The intrusion phases can be considered either as subtraction phases (solid solution of the III type) with respect to the metalloid, or as solid solutions of M intrusion into metal /66/. The first interpretation is based on the fact that these phases produce homogeneous systems over a comparatively wide interval of compositions /67/. However, as demonstrated by Makarov /68/, such contradistinction is hardly justifiable. He believes that they should be "incorporated into a single type of solid solutions with a variable number of atoms in the unit cell".

Proceeding from the fact that H solutions in Pd are the most typical representatives of these systems, Umansky /69/ puts forward the following surmise. In metals of transition groups, hydrogen, carbon, and nitrogen, which constitute with them intrusion phases, are to be found in the metallic state, i.e., "they surrender a part[1] of their valence electrons to the d-band of the crystal".

This inference can be substantiated by a series of facts. First of all it is important to indicate the sharp reduction of paramagnetism during the formation of the intrusion phases, which can be traced, for example, from the following data:

Phase	Zr	Zr,C	Zr,N	Ti	Ti,C	TiN	W	W,C
Susceptibility....	+91	-13	+30	+57	+4	+24	+52	+5

It is interesting to note that the more readily ionizable carbon[2]

1) More precisely, "the effective part".

2) The ionization potentials for C and N in relative units (1 is adopted for H) are equal to $I_C = 0.83$, and $I_N = 1.07$, respectively. For conversion into Kcal. per gram-atom they must be multiplied by 312.

reduces paramagnetism stronger than nitrogen. Thus, C and N, like H which was discussed earlier, are present in these phases in a partially ionized state.

The same is also evidenced by the high values of specific conductivity of such solid solutions, as well as their metallic luster. Noteworthy is the fact that in individual cases the formation of intrusion phases is accompanied even by a drop of the specific resistance with the preservation of the same sign of its temperature coefficient. To illustrate the above, the following data are hereby recorded:

Phase	V	V,C	V,N	Zr	Zr,C	Zr,N	Ti	Ti,C	Ti,N	Ta	Ta,C	Ta,N
Specific resistance $\rho \cdot 10^{-4}$ ohm.cm	0.07	1.56	0.86	0.45	0.63	0.14	0.90	1.93	0.22	0.15	1.0	1.35

Other circumstances also point to the ionized state of carbon and nitrogen. As is well known, the first ionization potentials of carbon, nitrogen, and hydrogen do not differ very much ($I_C : I_H : I_N = 0.83 : 1.00 : 1.07$). For this reason the collectivization of their valence electrons proceeds in close energy conditions.

Moreover, the deformation of the metal lattice during the intrusion of the metalloid leads to a reduction of the energy of the valence electrons, which fact creates favorable prerequisits for the filling of the d-band.

It is precisely this that explains the relatively great thermal effect of the formation of intrusion phases:

Metals		Ti	Zr	V	Mo	Ta
Thermal effect cal/mol	for nitrides	80000	82500	60000	-17000	58000
	for carbides	50000	5800	49500	- 4200	38000

The fact that the heats of nitride formation are higher than those for carbides is to be attributed to the correlation of the sizes of the metalloid atoms. Indeed $r_N > r_C$ which causes a greater deformation of the lattice during nitrogen intrusion.

Finally the considerable diffusion coefficients of carbon and nitrogen in these phases also indicate that these elements are in ionized state.

Actually the covalent radii of C, N, and O are quite close; they are equal to 0.77, 0.74, and 0.74 Å, respectively. Had these particles been existing in a monotypic form, one might have expected the diffusion coefficients to be approaching each other. However, they are far greater for C and N, than for O.

This fact emphasizes the singular status of C and N atoms: their high mobility both in the absence, and — in view of the foregoing — also in the presence, of an external electric field. In other words, they should be considered as small-size cations of a metal alloy.

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7. GENERAL CONCLUSIONS ON THE MODES OF METALLOID EXISTENCE.

The question dealing with the mode of the existence of metalloids dissolved in metals still remains in the very embryonic stage of solution. Within the scope of the technology of ferrous metals, the most important impurities of iron are known to be constituted by C, O, S, P, H, N, Si, Cr, Mn, Ni, and Co.

The preceding survey has shown that carbon, hydrogen and, probably, nitrogen are present in the solid and liquid iron - as well as Cr, Mn, Ni, and Co - primarily in the form of positively charged particles.

Oxygen, sulfur, phosphorus, and silicon, apparently exist in iron in a different state. Moreover, judging by the data pertaining to chemical equilibria, oxygen and sulfur are to be found in monatomic form. The small value of their diffusion coefficients imply that the sizes of these particles are comparatively large. It is natural then that they do not surrender their electrons to the d-band and do not form intrusion phases with metal.

On the basis of the fact that the electron cloud in the lattices of iron oxides and sulphides is shifted towards the metalloid, it is possible to assume that the mode of their existence approaches that of the anions (O^{2-}, S^{2-}). In particular, Kulikov, in comparing the heats of solution — approximately estimated by him — of the various forms of oxygen in liquid iron, comes to the conclusion that the most stable state in which oxygen is to be found in iron is the O^{2-} anion.

The very large sizes of O^{2-} and S^{2-}, as compared with the cations of carbon and nitrogen, hinder their movement and make it practically impossible for them to shift in the metal under the influence of the external electric field.

Like silicon, phosphorus occupies an intermediate position, since it is neither a cation, nor an anion, and forms particles with the atoms of Fe, in which a considerable role is played by homeo-polar bonds[1]. In respect to silicon, this is confirmed by the shape of the e.m.f. and surface tension curves, with regard to phosphorus - only by a break in the e.m.f. plots [71].

A further theoretical and experimental development of the problem will permit verification of these inferences and to reveal a number of additional characteristics. One of them already can be dwelt upon at this time. The matter concerns carbon.

The fact that carbon exists in metal in the form of a cation affords,

1) As is well known, the energy of loosening during the diffusion of phosphorus through iron (E = 46100 cal/mole [57]), is considerably smaller than during self-diffusion of iron (E = 69000 cal/mole [70]). This implies that the diffusion event occurs, in all probability, mainly between the phosphorus atoms which break the bonds with their neighbors and build a new environment composed of the particles of iron.

in particular, the explanation of the reason why it produces an intrusion phase with Gamma-iron, although this does not correspond to the relationship between their atomic radii (0.605, i.e., greater than 0.59).

In the solid phase of cementite the carbon ion is surrounded by six iron atoms. It is located in the octahedral pore of the Gamma-lattice. Yet, the coordination number of iron remains the same [12] as it was in pure metal.

Fe_3C is known to constitute a thermodynamically unstable phase. This ordered solid solution tends to decompose and separate graphite. Consequently, it is reasonable to expect, that in the liquid state — due to a lower energy of loosening[1] — in alloys with high contents of C, there should also appear, along with evenly distributed carbon atoms, groups of them similar to the elements of the graphite lattice.

Such incomplete molecular miscibility in eutectic melts was confirmed by x-ray diffraction studies described by Panilov and his co-workers in their works dealing with non-ferrous metals [18], [73], [74]. Bunin carried out a number of experiments which illustrate the possibility of polymerization of carbon atoms in liquid cast iron [75], [76].

A stream of cast iron diffused at the surface of ice water into minute droplets with a diameter up to 0.005 cm. The rate of cooling was estimated thereby at several thousand degrees per second. The increase of the degree of fragmentation, and consequently also the acceleration of the rate of freezing, resulted in a reduction of the contents of the precipitated graphite.

Yet, even in the minutest droplets graphite was steadily preserved in small quantities. Besides, it was also revealed that the graphite contents decreases with increased superheating of cast-iron. These facts provide a justification for Bunin to speak of the possibility of a heterophase fluctuation in liquid Fe-C alloys. In the limiting case it attains the sizes of the minutest particles of graphite.

It is clearly evident that such deviations from complete atomic miscibility are caused by a diversity of the interparticle forces.

Apparently, the interaction energy of the carbon atoms among themselves somewhat exceeds that between C and Fe. This causes the emergence of cybotactic groups, rich in carbon, and also facilitates the formation of graphitic heterophase fluctuations. It is possible that the latter in the initial form constitute the basic planes of the graphite lattice.

1) Samarin and Schwartzmann [72] on the basis of the data for cast iron viscosity determined the energy of loosening to be equal to 17600 cal. If one considers that the same magnitude also refers to diffusion, then it will appear to be far smaller than the energy of loosening for the solid state.

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Chapter VIII

INTERACTION OF LIQUID METAL AND SLAG.

The interaction processes of liquid metal with slag are of great technological significance. Innumerable investigations both of general and more specific character have been dedicated to the study of this phenomenon. It appears to be altogether impossible to embrace all these studies in the present chapter. Hence, it became necessary to confine this review only to a few most important problems. Considered as such are the electrochemical theory of interaction and the reactions of desulfurization, dephosphorization, and decarbonization.

I. ELECTROCHEMICAL THEORY OF INTERACTION OF LIQUID METAL (or MATTE) WITH SLAG.

It was revealed in the preceding chapters that the approach to liquid slags as to ionic solutions is more realistic than that of the molecular hypothesis, in that the former permits one to explain a greater number of experimental facts.

If this is so, then it is correct for the interaction of slags with liquid metals and mattes to be considered as electrochemical in character. Vanyukov [17] was the first to formulate this idea with respect to matte and slag in 1912.

GALVANIC CELLS AT HIGH TEMPERATURES.

Among the serious proofs supporting the idea of the electrochemical character of interaction between metal and slag is the experimental evidence pertaining to the existence of a jump in the electrochemical potential at the interface of the two liquid phases mentioned [27]. It consists in the construction of galvanic cells in which molten slag is the electrolyte. Moreover, liquid cast-iron, steel, ferrous alloys, or mattes, must be used to serve as cell electrodes in order to corroborate the electrochemical theory of the ferrous and non-ferrous pyrometallurgical processes.

From this point of view the work [37], in which CaO, Al_2O_3, and SiO_2 slag was used as electrolytes, with graphite and carborundum functioning as electrodes, is inconclusive since it leaves unanswered the question concerning the existence of the potential jump at the interface of molten ferrous and non-ferrous metals with slag. Apart from this, the very considerable distortions caused by the thermal electromotive force constituted the basic deficiency of the measurements.

Cells with Metallurgical Alloys of Various Concentration.

For the substantiation of the electrochemical theory in application to cast-iron and steel, the iron-carbon system was investigated as most important for the metallurgy of ferrous metals. A galvanic cell [47] composed of two liquid iron-carbon alloys (electrodes) was subjected to

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analysis with a varying concentration of C (from 0.2 to 4.7% C), and of a molten synthetic slag (electrolyte), containing 49% Al_2O_3, 43% CaO, and about 8% aluminum and calcium carbides. Schematically it could be represented as follows:

$$Fe,C\,|CaO,Al_2O_3,CaC_2,Al_4C_3|\,Fe,C \qquad \text{(VIII, 1)}$$

The arrangement of the cell is illustrated in fig. 163.

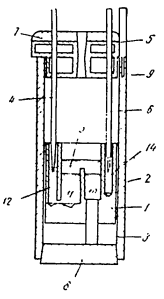

Fig. 163. Schematic diagram of the measuring cell:

1 - fused magnesium container; 2 - graphite tube; 3 - graphite rod; 4 and 5 - graphite conductors; 6 - tungsten-molybdenum thermocouple; 7 - fireclay lid; 8 - graphite stopper; 9 - magnesite packing; 10 - carbon alloys, 4% C; 11 - alloys with different carbon contents; 13 - slag; 14 - compartment for the thermocouple.

Since the concentration of iron ions in this type of slag is very low in comparison with the concentration of carbon ions, the cell functioned as a result of the difference in the activities of carbon in the metal alloys. The process which determined here the potential at both electrodes was probably as follows:

$$C^{2-}_{2\,(sl)} \rightleftharpoons 2C_{(met)} + 2\,\theta. \qquad \text{(VIII, 2)}$$

According to expectations, the electromotive force of the cell, measured at 1600°C, turned out to be the greater, the greater was the difference between the concentrations of carbon in the metal alloys (fig. 164). On the basis of its determined values, evaluations were made of ΔF of the free energy at 1600°C, during the solution of graphite in the alloys of

iron with carbon, and the activity of the latter at different concentrations. They proved to be approaching the figures found by different methods, namely by means of a study of chemical equilibria [5].

This fact confirms the correctness of the exposed theory as to the reasons for the display of differences in the potentials of the investigated cell, particularly so, if one considers that, according to the data obtained by non-electrochemical methods, the Fe-C melt deviates substantially from an ideal solution.

No less important then the Fe-C system for the metallurgy of ferrous metals are the alloys of iron with silicon. For this case a concentration cell was built of Fe-Si-C alloys and slag, containing 50% CaO, 10% MgO, and 40% SiO_2, as follows

$$Fe,\ Si,\ C\ |\ CaO,\ MgO,\ SiO_2\ \ Fe,\ Si,\ C. \qquad \text{(VIII, 3)}$$

The silicon contents in the alloys varied from 0.65 to 43%, while the concentration of carbon in all instances approached saturation. This fact, as well as the absence of iron ions in the slag and the high contents in it of silicon-oxide anions, justify the belief that the reason for the emergence here of the electromotive force is entirely due to the difference in the activities of silicon in the alloys.

Considering the slag composition and the probable absence from it of $Si_2O_7^{6-}$ anions [7], it appears to be possible to describe in the following manner the process which develops at both electrodes and determines the potential

$$Si_{(met)} + 3\,SiO_{4\,(sl)}^{4-} \rightleftharpoons \frac{4}{n}(Si_3O_9^{2-})_n + 4\theta. \qquad \text{(VIII, 4)}$$

The experiments were conducted at a temperature around 1470°C in order to avoid reduction reactions which become noticeable [8] in these conditions only upwards of 1500°C.

The curve plotted from these data and reflecting the dependence of the e.m.f. upon the concentration of silicon in the alloy (fig. 156) is composed of two branches separated by a sharp break at 50 atom. % Si. It is similar to the curve of potentiometric titration and points to the existence in the metal alloy of a sufficiently stable FeSi compound. This fact, as well as the character of the silicon activity dependence (determined from the e.m.f.) on Si concentration are in accord with the results obtained by other methods (heats of solution, chemical equilibria, surface phenomena) [9], [5], [10].

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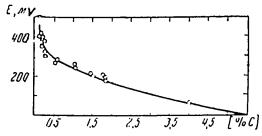

Fig. 164. Dependence of the e.m.f. of a high-temperature galvanic cell upon the concentration of carbon.

A similar galvanic cell was produced [11] for the Fe-C-P alloys which can be schematically represented as follows

$$\text{Fe, C, P} \mid \text{CaO, MgO, } SiO_2, Ca_3P_2, Mg_3P_2 \mid \text{Fe, C, P.} \qquad \text{(VIII, 5)}$$

One of its electrodes had a constant composition (in particular ~ 24% P), while in the second the concentrations of phosphorus varied from 1.5 to 23%. All alloys were carbon saturated. Slag served as the electrolyte, and contained 45% CaO, 14% MgO, 40% SiO_2 and around 0.5% phosphides. Measurements were effected at 1470°C. The following was apparently the process which determined the potential at both electrodes

$$P_{(met)} + 3\Theta \rightleftarrows P^{3-}_{(sl)}. \qquad \text{(VIII, 6)}$$

The cell's e.m.f. varied only with the activity ratio of phosphorus in the metal alloys.

The resulting curve (e.m.f. – phosphorus contents), like that for the Fe-Si-C alloys, shows a break (fig. 165) indicating that there exists a stable Fe_2P compound in metal. This agrees with the fusibility diagram for the Fe-P system, with the values of the heats of formation of iron phosphides [12], and the lack of electrolytic effect in these alloys [13].

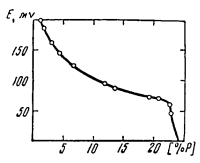

Fig. 165. Dependence of the e.m.f. upon the phosphorus contents in metal at 1470°C.

The cited facts confirm not only the existence of a jump of the electrochemical potential at the metal-slag interface for the most important metallurgical alloys of ferrous metals, but they also show that there are sufficiently stable groups of atoms, corresponding to FeSi and Fe_2P compounds, in cast-iron, steel, and ferrous alloys.

For non-ferrous pyrometallurgy the question of the existence of overvoltage at the matte-slag interface presents great interest. A whole series of concentration cells was prepared for this purpose [14]. Instead of multicomponent mattes, binary alloys of Pb-PbS, $Cu-Cu_2S$, $Ni_3S_2-Cu_2S$, and $FeS-Cu_2S$ were used as electrodes in them. Moreover, one of the electrodes was a sulfide with a constant composition (Cu_2S or PbS) while a melt with variable sulfur concentration constituted the other.

Instead of industrial slag containing highly aggressive iron silicate, glass composed of 72% SiO_2, 17% Na_2O, and 9% CaO was used to serve as electrolyte. Moreover, a quantity of Na_2S was added to the glass in a proportion of ~ 10% to the latter's weight. Thus, the e.m.fs were measured in galvanic cells

$$\begin{aligned} &\text{Pb, S} \mid Na_2O, CaO, SiO_2, Na_2S \mid PbS \\ &\text{Cu, S} \mid Na_2O, CaO, SiO_2, Na_2S \mid Cu_2S \\ &\text{Cu, Ni, S} \mid Na_2O, CaO, SiO_2, Na_2S \mid Cu_2S \\ &\text{Cu, Fe, S} \mid Na_2O, CaO, SiO_2, Na_2S \mid Cu_2S \end{aligned} \qquad \text{(VIII, 7)}$$

Experiments were carried out at temperatures ranging from 1180 – 1300°C.

The element, which in all cases determined the potential, was sulfur

$$S_{(met)} + 2\Theta \rightleftarrows S^{2-}_{(sl)}. \qquad \text{(VIII, 8)}$$

The results obtained by means of e.m.f. measurements coincide with the data produced by investigators who used methods other than electrochemical ones. In particular, in those systems where separation in two liquids ($Cu-Cu_2S$; Pb-PbS) was registered, the e.m.f. isotherms display a horizontal section.

As it may be seen from fig. 166 pertaining to the $Cu-Cu_2S$ system, the length of such a segment corresponds approximately to the extent of the separation region as reflected in the fusibility diagram. On the contrary, in cases where there is no separation ($FeS-Cu_2S$; $Ni_3S_2-Cu_2S$), the e.m.f. changes smoothly with the composition (see fig. 167).

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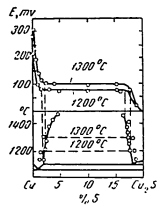

Fig. 166. Comparison of the fusibility diagram for the $Cu-Cu_2S$ system with the e.m.f. dependence upon the melt composition.

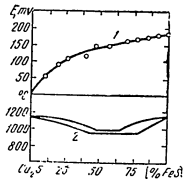

Fig. 167. Dependence of the e.m.f. upon the composition at 1180°C (1) and the fusibility diagram (2) of the Cu_2S–FeS system.

The activities of sulfur calculated from the e.m.f.s and according to the data for chemical equilibria [15] do not, as a rule, differ very much. For Pb–PbS and $Cu-Cu_2S$ melts the activity coefficients deviate hardly at all from unity (diluted solutions).

On the other hand, in Cu–Ni–S and Cu–Fe–S systems, where the atoms of the different metals differ by their binding energies with sulfur, the activity coefficient for the latter grows sharply (11 or 20 times) with rising concentration of the weakly interacting element (Fe or Ni, respectively). Finally the activity of sulfur in Cu_2S–FeS and Cu_2S–Ni_3S_2 alloys fails to obey the rule of additivity.

The cited regularities confirm Vanyukov's assumption concerning the electrochemical character of interaction between liquid mattes and slags and also shed additional light on the nature of sulfide melts. They indicate that the latter, while being semi-conductors, still approach metal alloys by their properties. The ion-atoms of these melts are not statistically evenly distributed in space. Some preferential groups of them may be found here, which cause the deviation from the laws of perfect solutions.

Cells with Slags of Different Composition.

The presence of a potential jump at the metal–slag interface is confirmed not only by the cells with alloys of varying concentration, but also by galvanic cells with slags of different composition.

Furthermore, if the above-cited investigations of the concentration cells of the amalgam type permitted establishing of the existence in liquid

metals of stable FeSi and Fe_2P compounds, then the study of the cells with a varying composition of slags enables one to reveal in the latter the presence of complex silicon-oxide anions. In order to determine whether all calcium silicates found in the solid state also remain in liquid slag, the following galvanic cell was constructed [17]

$$Fe, Si \mid CaO, SiO_2, Al_2O_3, MgO \mid C$$

or

$$MgO \mid CaO, SiO_2, Al_2O_3, MgO \mid Fe, Si, \qquad \text{(VIII, 9)}$$

the e.m.f. of which was determined only by the ratio of the silicon activities in both slags.

In order to avoid the emergence of diffusion potentials, the cell was made to constitute a concentration chain without transfer. It was composed of two chemical chains with slags of different composition, but with the same electrodes.

In each of these cells the energy developed as a result of the silicon formation reaction. Hence, the alloy containing silicon (Fe–Si) constituted one of its poles, while the other pole was formed by the oxygen electrode.

In a number of tests graphite was used to serve as the latter, because graphite is capable of retaining a certain proportion of combined oxygen even at high temperatures. In cases when slag is apt to be easily oxidized through contact with oxygen, or reduced by carbon, the oxygen electrode must be inert and resemble the so-called glass electrode which is being used in aqueous solutions. This condition in molten slags is apparently satisfied by solid magnesium oxide. At high temperatures it manifests an appreciable conduction and quite a definite activity of the oxygen which it contains.

As follows from fig. 168, measurements with graphite and magnesia electrodes produce similar results. Apparently, the errors caused by some degree or other of their irreversibility as oxygen electrodes are negligible.

Furthermore, the foregoing permits consideration of the transition cell [3] as being composed of oxygen (graphite) and silicon (carborundum) electrodes. Indeed, upon appropriate conversion, these data do not deviate too much from the section of the curve which refers to acid slags.

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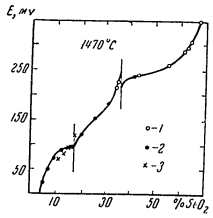

Fig. 168. Dependence of the e.m.f. on the contents of silicon:

1 - data for the magnesia electrode; 2 - same for graphite electrode; 3 - same according to the data recorded in /3/.

There are two inflections in the isotherm of e.m.f. (see fig. 168). Their presence indicates the existence in the melt (at 1470°C) of stable silicon-oxide anions of different degree of complexity. The first break corresponds to the composition where practically the entire oxygen, with the exception of the proportion used for the formation of AlO_2^-, is combined in the form of SiO_4^{4-} ion. The second break corresponds to metasilicate $MeSiO_3$, i.e., here silica is to be found mainly in the form of $(SiO_3^{2-})_n$ anions.

In view of the above, the first section of the curve characterizes the melt containing O^{2-}, AlO_2^-, and SiO_4^{4-} anions, whereas the second section pertains to liquid slag with AlO_2^-, SiO_4^{4-}, and $(SiO_3^{2-})_n$ anions.

As to the third section, the SiO_4^{4-} and AlO_2^- ions are absent from the melt; instead of them, along with the existing $(SiO_3^{2-})_n$, there appear here compound complexes of the $Si_xO_y^{z-}$ type, the composition of which is, apparently, variable.

Thus, the cited data not only confirm the electrochemical theory of interaction between metal and slag, but also point to the existence in the melt of anions of the Ca_2SiO_4 and $CaSiO_3$ compounds. On the other hand, compounds characteristic for their low stability in liquid state (which melt incongruently), for instance $Ca_3Si_2O_7$, do not manifest themselves in any appreciable way in the isotherms of electromotive forces.

POLARIZATION AND ELECTROCAPILLARY PHENOMENA.

The electrochemical theory is further substantiated by the polarization of the cell, i.e., the change of the difference of the electrode potentials depending on the strength of the flowing current. This phenomena was disclosed (fig. 169) in a voltaic cell (VIII, 3) composed of Fe-Si-C alloys /6/.

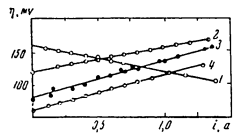

Fig. 169. Polarization of a galvanic cell at different concentrations (in atomic fractions) of silicon in its alloys with iron:

1 - anode $N_{Si} = 0.6$, cathode $N_{Si} = 0.025$; 2 - anode $N_{Si} = 0.10$, cathode $N_{Si} = 0.6$; 3 - anode $N_{Si} = 0.36$, cathode $N_{Si} = 0.6$; 4 - anode $N_{Si} = 0.43$, cathode $N_{Si} = 0.6$.

The investigation of polarization by commutation method showed that it was caused by slow diffusion of ions in metal. This is also supported by the fact that the angular coefficients of the polarization curves (reduced to common geometric characteristics) remain practically constant, in spite of a strong change of the composition of the metal alloys (from 2.5 to 43 atom.% Si), and depend on the composition of slag.

The existence of electrode potential and polarization lend confidence to the belief that the superposition of an external electric field may under favorable conditions cause a change of interphase tension at the metal-slag interface. Actually, such phenomena were revealed /16/ in the ferrous metal - slag system at temperatures of 1350-1500°C. For this purpose a method was used consisting in the determination of the size (per x-ray picture) of a liquid metal bead located under a layer of slag and subjected to cathodic and anodic polarization.

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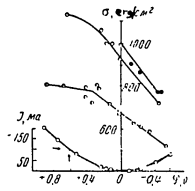

Fig. 170. Dependence of interphase tension σ at the Fe,C – slag interface from the jump φ of potential, and the curve of the strength of the polarizing current (I).

Electrocapillary phenomena were studied for iron alloys both with carbon and phosphorus in contact with slags composed of CaO, Na_2O, Al_2O_3 and SiO_2. A few of the electrocapillary curves obtained are displayed in fig. 170.

It was revealed thereby, both in the presence and in the absence of the external electric field, that the surface of the mentioned metal alloys is negatively charged, that the sodium ions at these interfaces possess a greater capillary activity then the ions of calcium, and that carbon adsorption falls, whilst that of phosphorus remains practically unchanged with growing negative value of the metal potential.

The foregoing provides still another confirmation of the electrochemical theory of interaction of ferrous metals with slags. Moreover, this offers an explanation, for example, of the influence exerted by the sign of the pole, carried to the electrode, upon the size of the metal beads separating from it during welding with direct current.

QUALITITATIVE PATTERN OF INTERACTION.

Let us now examine how the universally known phenomena observed during metal and slag interaction can be explained in terms of the electrochemical theory. We shall first dwell on the question why is it that the oxidizing power of slag cannot be determined in a simple form by all the oxygen ions existing in it.

Oxidizing Power of Slag.

Let us take a basic slag containing, say, CaO, MgO, FeO, and a small proportion of SiO_2, i.e., consisting of Ca^{2+}, Mg^{2+}, Fe^{2+}, O^{2-}, and Si_4^{4-} ions. Suppose it is brought into contact with molten liquid iron. Each type of the ions of slag will tend to pass partially into the metal phase.

This tendency will be determined by the difference in the binding energy of the particles with both phases and by temperature.

Since the binding energy of the oxygen ion with metal is sufficiently high, a fully measureable number of O^{2-} ions may penetrate into liquid iron.

$$O^{2-}_{(slag)} = O_{(met.)} + 2\,\theta \qquad \text{(VIII, 10)}$$

However, this will disturb the electro-neutrality of both phases. Owing to the shortage of negative ions, the slag will be charged positively and the metal negatively because of the presence of oxygen anions. Since excess charges in conductors are being expelled onto the surface, there will appear at the metal-slag interface a double electric layer and in connection with this a jump in the potential will manifest itself.

The existence of a double layer will impede the further migration of oxygen anions into liquid iron. If the interface surface is not too extensive (i.e., considerably smaller, for example, than in emulsions), then, as is evidenced in electrochemistry, a very small amount of excess charges will be sufficient to inhibit completely the transfer of O^{2-} anions. Consequently, their tangible macroscopic transfer will become possible only provided it is not accompanied by a further increase both of the density of the double layer envelope charge, and of overvoltage.

This condition materializes, in particular, when an equivalently charged number of some or other cations migrate from the slag into metal alongside with oxygen anions:

$$Me^{2+}_{(slag)} = Me_{(met.)} - 2\,\theta \qquad \text{(VIII, 11)}$$

This transfer is also facilitated by the arrangement of the double layer charges: the excess of positive ions in slag contributes to the expulsion from it of cations attracted by negative charges which abound in the metal.

According to the elelctromotive force series, the equilibrium concentration in liquid metal must be the greatest for cations of those metals which in the given system are relatively the highest. In the case under consideration these will be the cations of iron which actually accompany the migration of O^{2-} anions

$$Fe^{2+}_{(slag)} = Fe_{(met.)} - 2\,\theta \qquad \text{(VIII, 12)}$$

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Regardless of whether calcium[1] and magnesium are highly or weakly soluble in molten iron, their transfer into slag in appreciable quantities is impossible here. The position of Ca and Mg (highly base) in the electromotive series is such that they, while remaining in the metal, must expel the iron ions from slag and pass practically completely back into slag:

$$Ca_{(met)} + Fe^{2+}_{(sl)} \rightarrow Fe_{(met)} + Ca^{2+}_{(sl)}. \qquad \text{(VIII, 13)}$$

Thus, in the examined example only iron cations can accompany the transfer of oxygen anions into metal

$$Fe^{2+}_{(sl)} + O^{2-}_{(sl)} = Fe_{(met)} + O_{(met)}. \qquad \text{(VIII, 14)}$$

One should not presume, however, that in consequence of this the double layer and overvoltage will disappear. This will not occur because the tendencies for migration into metal of O^{2-} and Fe^{2+} ions (determinable by their binding energies with the phases) are different. If this tendency is stronger with O^{2-} than in Fe^{2+}, then a double layer will be formed with a negative charge in metal (and positive in slag), which will inhibit the transfer of O^{2-} and facilitate the migration of Fe^{2+}.

On the contrary, if the tendency towards migration in O^{2-} ions is weaker than in Fe^{2+}, then the arrangement of the charge signs in the double layer will be inverse (an excess of cations in metal, and of anions in slag) which will also equalize the transfer rates of both types of ions.

It becomes clear from the aforesaid that the oxidizing power of slag cannot be determined only by the concentration of all oxygen anions which exist in it. It also depends on the concentration in slag of the Fe^{2+} anions. If the latter are absent, then oxygen practically does not pass from slag into metal at all. Its transfer increases in proportion with the growth of the iron cation contents in slag.

The oxidizing power of slag depends therefore not only on its content of FeO, as follows from the molecular theory, but is simultaneously determined by the concentration of all oxygen ions and the concentration of iron ions. In other words, in the simplest of cases (without any allowance for the activity coefficient) the oxidizing power of slag must be measured not by the mole fraction of ferrous oxide N_{FeO}, but by the product of the ionic fractions of oxygen and iron, i.e., $N_{Fe^{2+}} \cdot N_{O^{2-}}$.

1) As shown by tests [17] with application of tracers (radioactive isotope Ca^{45}) the solubility of calcium in liquid iron saturated with carbon and covered by a layer of slag composed of CaO, Al_2O_3 and SiO_2 is inferior to the detection sensitivity of this method ($6 \cdot 10^{-5}$%).

Effect of Silica on Oxidizing Power of Slag.

Let us now consider the reason why the oxidizing action of slag for one and the same concentration of ferrous oxide declines upon the addition of silica.

Had there been no SiO_2 and other acid and amphoteric oxides contained in slag, i.e., if it consisted, for example, only of FeO, CaO, and MgO, then the concentration of oxygen ions in it would have been constant regardless of the changes in the contents of the individual components. The degree of the transfer of O^{2-} anions into metal would in this case be determined, as a first approximation, only by the concentration of Fe^{2+} ions in slag. More precisely (and this actually reflects the difference between the real slags and perfect solutions), the tendency towards migration would not be solely dependent on the ionic fraction of Fe^{2+}, but also on the concentration of other cations, inasmuch as they retain, with varying energy, the O^{2-} anions in slag.

The addition of silica leads to a considerable increase of the energy binding the oxygen ions with slag. In consequence thereof, even with a constant contents of FeO, the introduction of SiO_2 diminishes the tendency of O^{2-} anions to migrate into metal. This is to be attributed to the formation of sufficiently stable silicon-oxide anions resulting in a decrease of the O^{2-} ion concentration. For instance, in basic slags SiO_4^{4-} anions emerge upon the addition of SiO_2

$$SiO_2 + 2O^{2-} \rightarrow SiO_4^{4-}, \qquad \text{(VIII, 15)}$$

and in the general case - $Si_xO_y^{2-}$ ions.

$$x\,SiO_2 + (y - 2x)O^{2-} \rightarrow Si_xO_y^{2-}. \qquad \text{(VIII, 16)}$$

Thus, if in the molecular theory the effect of SiO_2 is attributed to a reduction in the degree of iron orthosilicate dissociation into molecules of free oxides

$$Fe_2SiO_4 \rightleftarrows 2FeO + SiO_2, \qquad \text{(VIII, 17)}$$

then, according to the ionic theory, it comes as a result of a drop of the oxygen anion concentration following the formation of silicon-oxide complexes.

Similar too is the action of other acid oxides (P_2O_5, TiO_2 and so on) as well as of Fe_2O_3, Al_2O_3 and their analogues, if they are present in the form of anions binding thereby the ions of oxygen.

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Desulfurizing Power of Slag.

We shall now consider the question of why the desulfurizing power of slag is primarily a function of the CaO contents in it.

If dissolved oxygen is absent in iron, then the transfer of S^{2-} anions from slag into metal, as in the case of O^{2-} ions, must be accompanied by a migration of Fe^{2+} cations. The introduction of CaO into slag weakens the migratory tendency of S^{2-} ions, in the first place, because the concentration of both S^{2-} and Fe^{2+} decreases, and in the second place, in view of the increasing penetration of O^{2-} anions into metal. The latter also demand the transfer of an equivalent number of Fe^{2+} cations, causing thus a reduction of the share of Fe^{2+} ions accompanying the S^{2-} anions during their passage into metal.

On the other hand, should the MnO contents be increased in slag, instead of CaO, then the concentrations of S^{2-} and Fe^{2+} ions would decrease as in the preceding case. However, since metallic manganese is closer to iron in the electromotive force series than calcium or magnesium, its cations, to a certain degree, might accompany the transfer of S^{2-} and O^{2-} anions into metal. This would weaken the effect of the second factor (pertaining to the reduction of the share of cations accompanying the anions of sulfur) and somewhat increase the chances of the S^{2-} anions to migrate into metal. In this respect the addition not of MnO, but of FeO, would be even more effective. Then the number of cations capable of accompanying the anions would not be changed at all.

If there is a definite concentration of dissolved oxygen in metal, then the charge compensation required for the macroscopic transfer of the sulfur anions may be achieved not only as a result of the migration of iron cations

$$Fe^{2+}_{(sl)} + S^{2-}_{(sl)} \rightleftarrows Fe_{(met)} + S_{(met)}. \qquad \text{(VIII, 18)}$$

A similar effect will be produced also by the transfer of oxygen anions in the reverse direction

$$S^{2-}_{(sl)} + O_{(met)} \rightleftarrows S_{(met)} + O^{2-}_{(sl)}. \qquad \text{(VIII, 19)}$$

The above equilibrium should be shifted more to the left, the weaker the bond between the oxygen anion and slag.

Since the O^{2-} ion is being retained firmly enough[1] by the Fe^{2+} cations, less solidly by Mn^{2+} cations, and comparatively weakly by Ca^{2+} ions (owing to the change of the cation radius), it would seem reasonable to expect that, at the same concentration of MeO, the equilibrium shift (VIII, 19) to the left should be the greatest for CaO, intermediate for MnO, and the least for FeO.

However, the bond stability of the S^{2-} anions also grows with the change from Ca^{2+}, to Mn^{2+} and Fe^{2+}. It is true though that the increase of interaction energy is somewhat less here than in the case of O^{2-} ions since their radius is smaller than that of S^{2-}. Yet, in spite of this, the examined equilibrium shifts but a little /18/ upon replacement of CaO_2 by MnO, and FeO in view of a simultaneous strengthening of the bonds of O^{2-} and S^{2-} ions with slag.

Oxidation of Impurities.

Let us turn now to the oxidation processes.

The elimination of carbon, silicon, and phosphorus will depend not only on the concentration of oxygen anions in slag, but also on the contents in it of iron cations. Indeed, in all these cases, on the one hand, as it may, for instance, be seen from the following possible transfer schemes[2]

$$C_{(met)} + O^{2-}_{(sl)} \rightleftarrows CO_{(gas)} + 2\theta, \qquad \text{(VIII, 20)}$$

$$Si_{(met)} + 4O^{2-}_{(sl)} \rightleftarrows SiO^{4-}_{4(sl)} + 4\theta, \qquad \text{(VIII, 21)}$$

$$P_{(met)} + 4O^{2-}_{(sl)} \rightleftarrows PO^{3-}_{4(sl)} + 5\theta. \qquad \text{(VIII, 22)}$$

the metal receives an excess negative charge. Hence, for a tangible macroscopic development of these processes, compensating transfers of Fe^{2+} cations from slag into metal are required.

On the other hand, the completeness of the shift of the mentioned equilibria will also be determined, apart from the concentration of oxygen anions, by their binding energy with the slag. The effect of the SiO_2 addition can be interpreted in two ways - either as a decrease of the concentration of O^{2-} ions, or as a strengthening of their bonds with the melt.

1) It should be borne in mind that the stability of ion bonds, in the first approximation, is determinable by their charges and by their radii according to the law of Coulomb. On the other hand, the interaction energy of the oxygen atoms will be greater with Ca atoms than with those of Fe. Such change in the arrangement of metals is due to the difference in the magnitude of ionization potentials, which can be easily demonstrated by means of thermodynamic cycle.

2) The schemes are given without any clear-cut factual indication as to the existence of FeSi and Fe_2P compounds.

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In either case the introduction of SiO_2 will contribute to the shifting of equilibria to the left. For silicon the shift in this direction becomes conspicuous only with considerable SiO_2 contents. In this case the reaction should be more correctly rewritten in the following form

$$Si_{(x+1)}O_{y\ (sl)}^{(z-4)-} + 4\theta \rightleftarrows Si_xO_{y\ (sl)}^{z-} + Si_{(met)}. \qquad \text{(VIII, 23)}$$

This direction if interaction, i.e., migration of Si from slag to metal, is more commonly known as the process of silicon restitution.

The dephosphorization reaction, as exhibited by tests, is more sensitive to the change of silica contents.

The substitution of one oxide by another changes only the binding energy of the oxygen anion with slag. Hence, the introduction of CaO instead of FeO, on the one hand, should contribute to the shifting of equilibrium to the right, for example (VIII, 22).

On the other hand, the reduction of the concentration of Fe^{2+} cations, which effect the charge compensation, will retard the oxidation reaction.

Consequently, there should exist an optimum correlation of FeO and CaO concentrations which is most advantageous for the elimination of the impurity from metal.

This situation was recently experimentally confirmed for phosphorus [19].

In limiting ourselves to these few examples, let us remark that the distribution of elements (iron, copper, nickel, cobalt, oxygen, and sulfur) between liquid mattes and slags, as well as in a number of other cases, can be examined in a similar way.

EQUILIBRIUM EQUATION.

Assuming that equilibrium establishes itself as a result of a correlated process of cation and anion distribution, let us formulate the general relationships on the basis of electrochemical thermodynamics.

To put it differently, in defining the conditions of equilibrium let us proceed from the experimentally established fact that the ions of each type, in distributing themselves between metal and slag, participate in the formation of a double electric layer and in the origination of overvoltage.

Supposing, for example, that there is a basic slag consisting of CaO, MgO, Fe^0, MnO, SiO_2, P_2O_5, and CaS, which is in a state of equilibrium with the metal containing Fe, Mn, Si, P, O, and S.

The general equations covering the distribution reactions of individual ions, or as more commonly referred to in electrochemistry - the

individual electrode processes - may be recorded schematically (without explicitly reflecting the presence of FeSi, Fe_2P and other compounds in metal) in the following manner:

$$Fe_{(sl)}^{2+} + 2\theta \rightleftarrows Fe_{(met)}, \qquad \text{(VIII, 24)}$$

$$Mn_{(sl)}^{2+} + 2\theta \rightleftarrows Mn_{(met)}, \qquad \text{(VIII, 25)}$$

$$O_{(sl)}^{2-} - 2\theta \rightleftarrows O_{(met)}, \qquad \text{(VIII, 26)}$$

$$S_{(sl)}^{2-} - 2\theta \rightleftarrows S_{(met)}, \qquad \text{(VIII, 27)}$$

$$SiO_4^{4-} + 4\theta \rightleftarrows Si_{(met)} + 4O_{(sl)}^{2-}, \qquad \text{(VIII, 28)}$$

$$PO_4^{3-} + 5\theta \rightleftarrows P_{(met)} + 4O_{(sl)}^{2-}. \qquad \text{(VIII, 29)}$$

These equations reflect only the initial and the final states, i.e., that which is indispensable for the determination of the equilibrium conditions, and which is usually insufficient for the identification of the mechanism and the kinetics.

The equilibrium difference of the potentials for each of the enumerated electrode processes will comprise respectively:

$$\varepsilon_{Fe} = \varepsilon_{Fe}^{\circ} + \frac{RT}{2F}\ln\frac{a_{Fe^{2+}}}{a_{Fe}}, \qquad \text{(VIII, 24')}$$

$$\varepsilon_{Mn} = \varepsilon_{Mn}^{\circ} + \frac{RT}{2F}\ln\frac{a_{Mn^{2+}}}{a_{Mn}}, \qquad \text{(VIII, 25')}$$

$$\varepsilon_{O} = \varepsilon_{O}^{\circ} + \frac{RT}{2F}\ln\frac{a_{O}}{a_{O^{2-}}}, \qquad \text{(VIII, 26')}$$

$$\varepsilon_{S} = \varepsilon_{S}^{\circ} + \frac{RT}{2F}\ln\frac{a_{S}}{a_{S^{2-}}}, \qquad \text{(VIII, 27')}$$

$$\varepsilon_{Si} = \varepsilon_{Si}^{\circ} + \frac{RT}{4F}\ln\frac{a_{SiO_4^{4-}}}{a_{Si}\cdot a_{O^{2-}}^4}, \qquad \text{(VIII, 28')}$$

$$\varepsilon_{P} = \varepsilon_{P}^{\circ} + \frac{RT}{5F}\ln\frac{a_{PO_4^{3-}}}{a_{P}\cdot a_{O^{2-}}^4}. \qquad \text{(VIII, 29')}$$

Since a single electric potential is being established for the state of equilibrium at the metal-slag interface, then

$$\varepsilon_{Fe} = \varepsilon_{Mn} = \varepsilon_{O} = \varepsilon_{S} = \varepsilon_{Si} = \varepsilon_{P} = \ldots = \varepsilon. \qquad \text{(VIII, 30)}$$

Hence, in equating the right sides of the recorded equations, we find the equilibrium conditions for various metallurgical interactions.

Thus, for instance, from equations (VIII, 24') and (VIII, 26') we obtain the coefficient of oxygen distribution

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$$L_O = \frac{a_{Fe^{2+}} \cdot a_{O^{2-}}}{a_{Fe} \cdot a_O} = \exp\left\{\frac{\epsilon^\circ_O - \epsilon^\circ_{Fe}}{RT} \cdot 2F\right\}, \qquad \text{(VIII, 31)}$$

and from expression (VIII, 24') and (VIII, 27') the same is derived for sulfur

$$L_S = \frac{a_{Fe^{2+}} \cdot a_{S^{2-}}}{a_{Fe} \cdot a_S} = \exp\left\{\frac{\epsilon^\circ_S - \epsilon^\circ_{Fe}}{RT} \cdot 2F\right\}. \qquad \text{(VIII, 32)}$$

A combining of the relationships (VIII, 24') and (VIII, 25') gives the equilibrium constant for the reaction of manganese

$$K_{Mn} = \frac{a_{Fe} \cdot a_{Mn^{2+}}}{a_{Mn} \cdot a_{Fe^{2+}}} = \exp\left\{\frac{\epsilon^\circ_{Fe} - \epsilon^\circ_{Mn}}{RT} \cdot 2F\right\}, \qquad \text{(VIII, 33)}$$

while the same for relationships (VIII, 24') and (VIII, 29') produces the equilibrium constant for the reaction of dephosphorization

$$K_P = \frac{a^5_{Fe} \cdot a^2_{PO_4^{3-}}}{a^2_P \cdot a^8_{O^{2-}} \cdot a^5_{Fe^{2+}}} = \exp\left\{\frac{\epsilon^\circ_{Fe} - \epsilon^\circ_P}{RT} \cdot 10F\right\}. \qquad \text{(VIII, 34)}$$

Without dwelling on other possible expressions, we shall only note the result of the comparison of equations (VIII, 26') and (VIII, 27')

$$K_{O.S} = \frac{a_{O^{2-}} \cdot a_S}{a_O \cdot a_{S^{2-}}} = \exp\left\{\frac{\epsilon^\circ_O - \epsilon^\circ_S}{RT} \cdot 2F\right\}. \qquad \text{(VIII, 35)}$$

If the concentration of a substance dissolved in iron is not large, then (according to the theory of infinitely dilute solutions) the activity of this admixture can be approximatively replaced by percentage in weight, whereas the activity of the solvent a_{Fe} may be assumed to be equal to unity. In this case the equation will include by way of unknown quantities only the activity of the ions in slag. In order to pass from them to the concentrations, either experimentally established ratios, or reference to the quantitative theory of slags[1] is required.

In those cases where the metal phase cannot be considered as infinitely dilute solution (cast-iron, special steels, ferrous alloys, mattes) the substitution of activity by weight percentage becomes inadmissible. Along

1) From the words of semi-empirical character; see, for example, [27], [27].

with experimental studies of the degree of the metal phase deviation from the ideal solution, there arises a need for the development of a quantitative theory for such solutions.

ELECTROMOTIVE FORCE SERIES.

As may be seen from the equations recorded above, the equilibrium conditions, i.e., the distribution coefficients and equilibrium constants, may be found experimentally, and not only by routine chemical methods, but also by means of e.m.f. measurements.

A further development and more precise elaboration of the measurement procedure [4], [6], [7], [11], [14] will permit the production of an electrochemical series of electromotive forces for liquid slags, if the normal potential for oxygen ϵ°_O or iron ϵ°_{Fe}, for example, be taken for a standard.

On the other hand, the electromotive series for molten slags, i.e., a selection of magnitudes of normal potentials of elements (Mn, O, Si, S, P, Al, etc.) with respect to that for iron (or oxygen) could be calculated according to the above-mentioned equations from the distribution coefficients and equilibrium constants determined by regular methods other than electrochemical.

Thus, for instance, if for reactions

$$\left.\begin{aligned} Me'_{(met)} + Me''O_{(sl)} &\rightleftarrows Me'_{(met)} + Me''O_{(sl)} \\ Me'_{(met)} + Me'_2O_{(sl)} &\rightleftarrows 2\,Me'_{(met)} + Me''O_{(sl)} \end{aligned}\right\} \qquad \text{(VIII, 36)}$$

one should make use of the experimental data [20] for the equilibrium "constants" calculated on the basis of the ideal law of mass action

$$K = \frac{(Me''O)\,[Me']}{(Me'O)\,[Me'']}; \quad K_1 = \frac{(Me''O)\,[Me']^2}{(Me'_2O)\,[Me'']}, \qquad \text{(VIII, 37)}$$

then, for example, from the equation

$$\epsilon^\circ_{Me''} - \epsilon^\circ_{Me'} = 0{,}0001\,T \lg K, \qquad \text{(VIII, 38)}$$

which is analogous to expression (VIII, 38) it would become possible to evaluate the difference of the standard potentials for molten oxides, i.e., the quantity $(\epsilon^\circ_{Me''} - \epsilon^\circ_{Me'})$ required for the compilation of an electromotive force series.

A comparison is made in table 22 of the values $(\epsilon^\circ_{Me''} - \epsilon^\circ_{Me'})$ calculated in this manner with the corresponding values for aqueous solutions and molten chlorides [21]. In the latter case the data for ϵ°_{Fe} were lacking, in view of which, for the purposes of comparison, the ratio was taken for oxides of equilibrium "constants" for interaction reactions

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of various metal oxides with iron.

It can be seen from this tabulation that the sequence order and the sign of the difference of potentials remained the same in each of the three series, with the exception of the Ni, Co pair. The potentials of the latter for aqueous solutions differ very little. Consequently a small difference in the temperature coefficients could easily change their position in the series with a rise in temperature. The absolute values of the difference of the standard potentials for the oxide and chloride melts approach each other and change regularly with increasing temperature.

Table 22. Comparison of differences of the standard potentials for aqueous solutions and molten oxides and chlorides.

Me'	Me"	$(\epsilon^{o}_{Me"} - \epsilon^{o}_{Me'})$ v, at the temperature °C of			
		Oxides		Chlorides	Aqueous solutions,
		1600	1200	700	25
Mn^{2+}	Fe^{2+}	—	+0,51	—	+0,66
Ni^{2+}	Co^{2+}	−0,10	−0,08	+0,06	−0,007
Co^{2+}	Fe^{2+}	—	−0,25	—	−0,18
Ni^{2+}	Fe^{2+}	—	−0,33	—	−0,19
Cu^{2+}	Fe^{2+}	—	−0,56	—	−0,96
Mn^{2+}	Cu^{2+}	+0,96	+1,07	+1,15	—
Mn^{2+}	Ni^{2+}	+0,80	+0,84	+0,86	—

Similar calculations may be effected also for other elements, provided the corresponding values of L_i and K_i are known.

KINETICS OF METAL AND SLAG INTERACTION

Introductory Remarks.

The advantages of the ionic theory become conspicuously evident when one examines such phenomena as cannot be explained by the molecular hypothesis. Listed herein should be, for instance, good electrical conductance of liquid slags, their electrolysis, the existence of over-voltage at the metal-slag interval, electrocapillary phenomena, and the special form of the equilibrium laws (replacement of the activity of a compound by the product of the activities of its ions). No doubt, similar phenomena should also be expected to appear in the domain of the kinetics of metal and slag interaction.

Under definite conditions the intensity of interaction may, as is well known, be limited by the rate of any of its stages. At the present time the difference of the ionic theory from the molecular in matters related to kinetics can be demonstrated with the least difficulty in those cases when the penetration of the metal-slag boundary constitutes a process determining

the rate [22].

Indeed, according to the molecular hypothesis there occurs an exchange of uncharged particles between these phases. Moreover, apart from the adsorption field, it is not necessary to take into account any other fields at the metal-slag interface. Furthermore, if the substances which take part in the transfer form dilute solutions, then the rates of the processes are directly proportional to their concentrations in the corresponding phases.

On the contrary, according to the ionic theory it is charged particles which migrate across the phase boundary. Thus, for instance, as a result of carbon, silicon, and phosphorus combustion, oxygen ions pass from slag into the metal; sulfur ions move in the opposite direction during desulfurization; in the process of deoxidation and alloying it is the ions of the added elements which migrate, and so on. The fact to be considered in all these cases is that there appear excess charges in metal and slag, while a jump of the electric potential occurs at the phase interface.

The latter would have rapidly stopped these migrations, had no other processes been developing along with them which liquidate the further accumulation of charges. Among these processes the following should be mentioned in particular - migration of iron ions from slag to metal and back, reduction of the trivalent iron ions to divalent, movement of the oxygen ions from metal to slag, and so on.

As a result of this the macroscopic process which actually takes place constitutes a combination of two such stages, with the following possible alternatives:

1) simultaneous migration of cations and anions in the same directions, e.g.,

$$\begin{array}{l} Fe^{2+}_{(sl)} + 2\ominus \rightarrow Fe_{(met)} \\ O^{2-}_{(sl)} - 2\ominus \rightarrow O_{(met)} \\ \hline Fe^{2+}_{(sl)} + O^{2-}_{(sl)} \rightarrow Fe_{(met)} + O_{(met)}, \end{array} \qquad \text{(VIII, 39)}$$

2) of anions in different directions

$$\begin{array}{l} S_{(met)} + 2\ominus \rightarrow S^{2-}_{(sl)} \\ O^{2-}_{(sl)} \rightarrow O_{(met)} + 2\ominus \\ \hline S_{(met)} + O^{2-}_{(sl)} \rightarrow S^{2-}_{(sl)} + O_{(met)}, \end{array} \qquad \text{(VIII, 40)}$$

3) of cations in opposite directions

$$\begin{array}{l} Mn_{(met)} - 2\ominus \rightarrow Mn^{2+}_{(sl)} \\ Fe^{2+}_{(sl)} + 2\ominus \rightarrow Fe_{(met)} \\ \hline Mn_{(met)} + Fe^{2+}_{(sl)} \rightarrow Mn^{2+}_{(sl)} + Fe_{(met)}, \end{array} \qquad \text{(VIII, 41)}$$

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4) combining of the trivalent iron reduction events with the migration of anions

$$\frac{\begin{array}{c}2FeO_{2\,(sl)}^{-}+2\theta \rightarrow 2Fe_{(sl)}^{2+}+4O_{(sl)}^{2-}\\ O_{(sl)}^{2-}-2\theta \rightarrow O_{(met)}\end{array}}{2FeO_{2\,(sl)} \rightarrow 2Fe_{(sl)}^{2+}+3O_{(sl)}^{2-}+O_{(met)}}, \qquad \text{(VIII, 42)}$$

5) same in conjunction with the transfer of cations

$$\frac{\begin{array}{c}2FeO_{2}^{-}+2\theta \rightarrow 2Fe_{(sl)}^{2+}+4O_{(sl)}^{2-}\\ Mn_{(met)}-2\theta \rightarrow Mn_{(sl)}^{2+}\end{array}}{2FeO_{2}^{-}+Mn_{(met)} \rightarrow 2Fe_{(sl)}^{2+}+Mn_{(sl)}^{2+}+4O_{(sl)}^{2-}}. \qquad \text{(VIII, 43)}$$

The presence in one process of the two stages mentioned, and the existence at the phase interface of overvoltage affecting substantially the development of these stages, impose a singular imprint on the aspect of the kinetic equations distinguishing it somewhat from the one pertaining to the transfer of uncharged particles.

We shall deal in detail only with one of the unemerated cases, since the analysis is similar in every respect for all other alternatives. Let us consider the combination (VIII, 40), i.e., the transfer of sulfur and oxygen in different directions. Preference was given to this alternative in view of the experimental material available for subsequent comparison with the regularities determined.

Deduction of Kinetic Equations

Let us assume that sulfur ions migrate from metal to slag, while the subsequent accumulation of charges in both phases and the increase of the potential jump at the interface is eliminated by the inverse movement of the oxygen ions.

Since the process is in development, the equilibrium potentials of sulfur $\epsilon_{p,S}$ and oxygen $\epsilon_{p,O}$, corresponding to their activities a_i in both phases, are still to be attained. They can be represented by equations

$$\varepsilon_{p.\,S} = \varepsilon_S^{\circ} + \frac{RT}{2F} \ln \frac{a_S}{a_{S^{2-}}}, \qquad \text{(VIII, 44)}$$

$$\varepsilon_{p.\,O} = \varepsilon_O^{\circ} + \frac{RT}{2F} \ln \frac{a_O}{a_{O^{2-}}}, \qquad \text{(VIII, 45)}$$

in which ϵ_S° and ϵ_O° = standard potentials of sulfur and oxygen;

R = gas constant, joule/degree;
T = absolute temperature;
F = 96500 Coulombs.

At any given moment throughout the process there arises some single potential ϵ at the phase interface. It differs from the equivalent potentials

$$\varepsilon = \varepsilon_{p.\,S} - \eta_S = \varepsilon_{p.\,O} + \eta_O \qquad \text{(VIII, 46)}$$

by quantities η_S and η_O.

The latter were assumed to have different signs for the following reason. For a directed transfer of sulfur from metal to slag, it is necessary to diminish the potential as compared to the equilibrium ones. In other words, the density of the positive charge in the metallic envelope of the double layer must be reduced. On the contrary, for the migration of oxygen ions from slag to metal an increase is required of the potential over the equilibrium potential, i.e., intensification of the density of the positive charge in metal. It follows directly from the above that the signs of η_S and η_O should be different.

The constant accumulation of charges discontinues with the establishment of a steady macroscopic process. The ions, which move more rapidly, accelerate the migration of those which move slowly, while the latter slow down the movement of the former. Therefore, the transfer rates of sulfur and oxygen ions are equal at any given moment

$$v = \vec{v}_S = \overleftarrow{v}_O. \qquad \text{(VIII, 47)}$$

The mathematical expression for the rates of such transfers was developed in electrochemistry relatively long ago [23]. Furthermore, it was applied to the analysis of similar processes, namely to the solution of sodium from amalgam

$$\frac{\begin{array}{c}Na_{(Hg)} \rightarrow Na_{(p-p)}^{+}+\theta\\ H_{(p-p)}^{+}+\theta \rightarrow \frac{1}{2}H_{2,\,gas}\end{array}}{Na_{(Hg)}+H_{(p-p)}^{+} \rightarrow Na_{(p-p)}^{+}+\frac{1}{2}H_{2,\,gas}}$$

and in general to the corrosion of metals and alloys by aqueous aggressive media [24].

By utilizing these expressions we obtain for the processes under review

$$v = \vec{v}_S = k_{1,S}[S] \exp\left\{-\frac{(\varepsilon_{p.\,S}-\eta_S)\,2F\alpha_{1,S}}{RT}\right\} - k_{2,S}(S^{2-}) \exp\left\{\frac{(\varepsilon_{p.\,S}-\eta_S)\,2F\alpha_{2,S}}{RT}\right\} \qquad \text{(VIII, 48)}$$

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and

$$v = \overleftarrow{v_O} = k_{2,O}(O^{2-}) \exp\left\{\frac{(\epsilon_{p,O} + \eta_O) 2F\alpha_{2,O}}{RT}\right\} - k_{1,O}[O] \exp\left\{-\frac{(\epsilon_{p,O} + \eta_O) 2\alpha_{1,O} F}{RT}\right\}. \quad \text{(VIII, 49)}$$

Here $\underline{/S/}$ and $\underline{/O/}$ = atomic fractions of sulfur and oxygen in metal;
(S^{2-}) and (O^{2-}) = their ionic fractions in slag;
α_i = constant coefficients, depending on the correlation of the interaction energy of a given particle with both phases (more precisely upon the shape of the potential curves at the point of their intersection), whereupon according to the deduction

$$\alpha_{1,S} + \alpha_{2,S} = 1 \quad \text{and} \quad \alpha_{1,O} + \alpha_{2,O} = 1; \quad \text{(VIII, 50)}$$

$k_{1,S}$ and $k_{2,S}$ are the constants of the direct and inverse reactions rates,

$$S_{(metl)} + 2\theta = S^{2-}_{(sl)}.$$

They include the energy of activation E of the corresponding event

$$k_{i,S} = k^{\circ}_{i\,S} \exp\left\{-\frac{E_{i,S}}{RT}\right\}. \quad \text{(VIII, 51)}$$

The same applies to the rate constants $k_{1,O}$ and $k_{2,O}$ of the reaction

$$O_{(metl)} + 2\theta = O^{2-}_{(sl)}.$$

Since the transfer is realized by the particles located at the phase boundary, it is determined, in the first place, by their concentrations in the adsorption layer.

Because the contents of sulfur and oxygen in metal, and of their ions in acid slags, is usually small, one may consider that the adsorption layer, is far from being saturated, as far as they are concerned. In other words, the concentrations of these substances in it are directly proportional to the volume concentrations. The factors of proportionality are included in the quantities $k_{i,O}$ and $k_{i,S}$.

To find the explicit form of dependence of v upon the composition and

temperature, it is necessary to exclude $\epsilon_{p,S}$, $\epsilon_{p,O}$, η_S and η_O from equations (VIII, 48) and (VIII, 49). We shall first substitute in formula (VIII, 48) the value of $\epsilon_{p,S}$ from expression (VIII, 44). At the same time we shall replace the activities of S and S^{2-} by the products of concentration by the activity coefficient, for example,

$$a_S = \gamma_S [S]. \quad \text{(VIII, 52)}$$

Then, considering that $\eta = 0$ when $v = 0$, we find, after a number of modifications, that

$$v = \vec{v_S} = k_S [S]^{\alpha_{2,S}} (S^{2-})^{\alpha_{1,S}} \left[\exp\left\{\frac{2F\eta_S}{RT} \cdot \alpha_{1\,S}\right\} - \exp\left\{-\frac{2F\eta_S}{RT} \cdot \alpha_{2,S}\right\}\right]. \quad \text{(VIII, 53)}$$

Here

$$k_S = k_{1,S} A^{\alpha_{1,S}} = k_{2,S} A^{-\alpha_{2,S}}; \; A = \frac{\gamma_{S^{2-}}}{\gamma_S} \exp\left\{\frac{2F\epsilon^{\circ}_S}{RT}\right\}. \quad \text{(VIII, 54)}$$

Proceeding in a similar manner with $\epsilon_{p,O}$ and the equation (VIII, 49) we have

$$v = \overleftarrow{v_O} = k_O [O]^{\alpha_{2,O}} (O^{2-})^{\alpha_{1,O}} \left[\exp\left\{\frac{2F\eta_O}{RT}\alpha_{2,O}\right\} - \exp\left\{-\frac{2F\eta_O}{RT}\alpha_{1,O}\right\}\right], \quad \text{(VIII, 55)}$$

where

$$k_O = k_{1,O} B^{\alpha_{1,O}} = k_{2,O} B^{-\alpha_{2,O}}; \quad B = \frac{\gamma_{O^{2-}}}{\gamma_O} \exp\left\{-\frac{2F\epsilon^{\circ}_O}{RT}\right\}. \quad \text{(VIII, 56)}$$

In passing over to the replacement of η_S and η_O, we determine their interrelation from equations (VIII, 44), (VIII, 45), and (VIII, 46)

$$\eta_O = -\eta_S + \epsilon^{\circ}_S - \epsilon^{\circ}_O + \frac{RT}{2F} \ln \frac{[S](O^{2-})}{[O](S^{2-})} + \frac{RT}{2F} \ln \frac{\gamma_S \gamma_{O^{2-}}}{\gamma_O \gamma_{S^{2-}}} \quad \text{(VIII, 57)}$$

and substitute for η_O in formula (VIII, 55) its value from expression

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(VIII, 57). Then

$$v = \overleftarrow{v}_O = k_O \left[\left(\frac{B}{A} \cdot \frac{[S]}{(S^{2-})} \right)^{\alpha_{2,O}} (O^{2-}) \exp\left\{ -\frac{2F\eta_S}{RT} \alpha_{2,O} \right\} - \right. \\ \left. - \left(\frac{A}{B} \cdot \frac{(S^{2-})}{[S]} \right)^{\alpha_{1,O}} [O] \exp\left\{ \frac{2F\eta_S}{RT} \alpha_{1,O} \right\} \right]. \qquad \text{(VIII, 58)}$$

The system of two equations (VIII, 53) and (VIII, 58) permits one in principle to exclude η_S and to express the rate of the process v through concentrations and temperature. However, inasmuch as all α_i are usually[1] proper fractions, it appears to be impossible to do so in a general way. The problem is to be solved for every particular case separately when the values for all i are predetermined.

By way of an example, let us find the solution for the case, when

$$\alpha_1 = \alpha_{1,S} = \alpha_{1,O}, \qquad \text{(VIII, 59)}$$

and, consequently,

$$\alpha_2 = \alpha_{2,S} = \alpha_{2,O}. \qquad \text{(VIII, 60)}$$

This assumption can be substantiated in a certain measure by the similarity of a number of sulfur and oxygen properties. The possibility, therefore, is not excluded that if not the absolute values of these particles, then at least the relationship of their interaction forces with both phases, are approaching each other.

Upon this assumption, equation of the expressions for v given in formulas (VIII, 53) and (VIII, 58) permits reducing the exponential containing $\eta_S \alpha_2$, and determining the exponential including η_S without α_i. Upon exclusion of this exponential from equation (VIII, 53), and after a series of modifications, we find the unknown relationship between the rate and the phase compositions

$$v = \frac{\frac{k_{2,O}}{k_{2,S}} k_S (O^{2-}) [S] - k_S \frac{k_{1,O}}{k_{1,S}} [O] (S^{2-})}{\left\{ [S] + \frac{k_{1,O}}{k_{1,S}} [O] \right\} \cdot \left\{ (S^{2-}) + \frac{k_{2,O}}{k_{2,S}} (O^{2-}) \right\}^{\alpha_2}}. \qquad \text{(VIII, 61)}$$

1) With reference to the possible values of α, see /25/.

Certain Conclusions Resulting from the Kinetic Equation.

Supposing the concentration of oxygen in metal is constant for each given temperature. Then equation (VIII, 61) may be rewritten as follows

$$v = \frac{a - bx}{(a_1 + x)^{\alpha_2}}. \qquad \text{(VIII, 62)}$$

Here $x = (S^{2-})$, whereas the remaining quantities are grouped within the parameters a, a_1 and b.

It follows from expression (VIII, 62) that v drops with increasing x. Moreover, it is easy to see that not only

$$\frac{\partial v}{\partial x} < 0, \qquad \text{(VIII, 63)}$$

but also

$$\frac{\partial^2 v}{\partial x^2} > 0. \qquad \text{(VIII, 64)}$$

In other words, the fall of rate v of the desulphurization process is retarded with the growth of concentration x of sulfur in slag.

Let us deal now with the second characteristic. From equation (VIII, 61) it transpires that the initial rate which complies to the condition

$$(S^{2-}) = x = 0, \qquad \text{(VIII, 65)}$$

may be represented by the formula

$$v_0 = \frac{a}{a_1^{\alpha_2}} = \frac{k_S [S]}{\left\{ [S] + \frac{k_{1,O}}{k_{1,S}} [O] \right\}^{\alpha_2}} \cdot \left(\frac{k_{2,O}}{k_{2,S}} \right)^{\alpha_2} \cdot (O^{2-})^{\alpha_2}. \qquad \text{(VIII, 66)}$$

It may be seen from the above that the rate of the direct reaction increases not only with the contents of sulfur in metal, but also with the concentration of oxygen ions in slag, i.e., with its basicity. This deduction is valid for all cases, with the exception of the one when $\alpha_1 = 0$ (i.e. $\alpha_2 = 1$).

The third peculiarity refers to the tangent of the curve v(x). Its expression is produced by differentiation of equation (VIII, 62)

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$$\frac{\partial v}{\partial x} = v'_x = -\frac{[a_1 b + a_2 a + b(1 - a_2)x]}{(a_1 + x)^{1+a_2}}. \qquad \text{(VIII, 67)}$$

At the initial instant of time

$$v'_{x\to 0} = -\frac{a_1 b + a_2 a}{a_1^{1+a_2}} = \frac{k_S\left\{a_2[S] + \frac{k_{1,O}}{k_{1,S}}[O]\right\}\left(\frac{k_{2,S}}{k_{2,O}}\right)^{a_2}}{\left\{[S] + \frac{k_{1,O}}{k_{1,S}}[O]\right\}^{a_1}(O^{2-})^{a_2}}. \qquad \text{(VIII, 68)}$$

This relationship shows that the quantity $(-v'_{x\to 0})$ is inversely proportional to (O^{2-}). In other words, the drop of the process rate at the initial moment is the greater, the less the concentration of oxygen ions in slag, i.e., the lower its basicity. Let it be noted that this conclusion is true when α_2 is not equal to zero $(\alpha_1 \neq 1)$.

The fourth singularity consists in the following. From expression (VIII, 66) — if the small addend in the denominator which contains /0/ be disregarded — it transpires that the rate constant of the direct reaction (at the initial moment) may be represented, considering equations (VIII, 54) and (VIII, 56), in the following aspect

$$k_1 = k_S\left(\frac{k_{2,O}}{k_{2,S}}\right)^{a_1} = k_{2,S}^{a_1} A^{-a_1} k_{2,O}^{a_1} = k_{1,S}^{a_1} k_{2,O}^{a_1}. \qquad \text{(VIII, 69)}$$

Whence, and from expression (VIII, 51), it follows that the seeming activation energy of the direct reaction is composed of the energies of activation $E_{1,S}$ - of the sulfur transfer from metal to slag, and $E_{2,O}$ - of the oxygen ions migrating in the opposite direction, or more precisely

$$E_1 = a_2 E_{1,S} + a_1 E_{2,O}. \qquad \text{(VIII, 70)}$$

Since $E_{2,O}$ depends on the stability of the bond of O^{2-} ions with slag, and it, in turn, is lower the greater the basicity, then it may be expected that the activation energy of the desulfurization process will decrease with growing basicity of slag.

2. DESULFURIZATION REACTION.

During the smelting of ferrous metals with charge materials, a certain proportion of sulfur, as a rule, is introduced, which lowers the quality of production. Consequently, a necessity arises in a number of cases for measures to be taken which would assure the elimination of sulfur. They are applied either during the metal smelting process or through ex-furnace processing.

The first method is universally applied in steel production by basic processes. In cast-iron smelting, ex-furnace procedures are also used sometimes to remove sulfur in addition to the proportion eliminated into slag during the smelting cycle. Listed among these methods should be the treatment of cast-iron in the ladle by means of various reagents extracting sulfur and often containing salts of alkali metals.

In the process of metallurgical smelting the metal interacts with slag and furnace gases as a result of which an exchange of sulfur takes place between these three phases.

According to the opinion of a number of investigators, sulfur in appreciable quantities passes into metal from furnace gases when sulfurous fuel is being used. For this reason it seems to be interesting to consider the interaction of metal both with the gaseous phase and with slag.

INTERACTION OF IRON WITH GASES CONTAINING SULFUR.

The reactions of gaseous H_2S and SO_2 with liquid metal are not only of technological importance. They are broadly used in the study of the properties of Fe-S melts. This refers particularly to the activity of sulfur dissolved in metal. The application of the method based on the determination of the dependence of the equilibrium composition of the melt on the temperature and the partial pressures of the reacting gases is most widespread.

Reaction with Hydrogen Sulfide.

To determine the activity of sulfur in iron the equilibrium of reaction

$$S_{Fe} + H_{2,(gas)} = H_2S_{(gas)}. \qquad \text{(VIII, 71)}$$

is investigated.

The selection of this reaction is based on the relative ease with which equilibrium can be established, on the reversibility of the reaction, and the commensurability of the concentrations of all substances which permits the production of fairly accurate results by routine analytical methods.

In spite of this, the data of different investigators disagree to a considerable extent, which fact should be attributed to measurement errors. Some authors /26/, /27/, for example, failed to take measures to eliminate thermal diffusion which modifies substantially the composition of gas near

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the metal surface.

Britzke and Kapustinsky /28/ were the first to demonstrate that the effect of thermal diffusion is especially noticeable in the case of gas mixtures possessing different densities. This, in particular, concerns the mixture of H_2 and H_2S in which an appreciable separation of components may ensue in consequence of thermal diffusion. Additional errors arise /26/ in view of the inhomogeneity of the temperature field, manifested during heat-treatment of metal in the induction furnace.

The narrowness of the temperature interval contributes to the errors /26/ because it reduces the reliability of the obtained equilibrium constant versus temperature relationship. Also responsible for the discrepancies is the existence in metal of appreciable concentrations of silicon (2-3%). The presence of the latter considerably increases the activity of sulfur.

Some authors /30/ in the study of reaction equilibrium (VIII, 71) applied the method of the jet, adopted earlier in the work by Britzke and Kapustinsky /28/. The data obtained thereby refer mostly to the highly sulfurous alloys (up to 37% S) and embrace a fairly wide temperature range (from 860 to 1530°C).

As may be seen from fig. 171, the results pertaining to pure FeS are close to those established earlier by Britzke and Kapustinsky. Moreover, the temperature dependence of the equilibrium constant proposed for this composition

$$\lg K = \lg \frac{p_{H_2S}}{p_{H_2}} = -\frac{3025}{T} + 0{,}873 \qquad \text{(VIII, 72)}$$

does not differ practically from Britzke-Kapustinsky's equation

$$\lg K = \lg \frac{p_{H_2S}}{p_{H_2}} = -\frac{3070}{T} + 0{,}940, \qquad \text{(VIII, 73)}$$

although the latter was obtained for a narrower temperature interval.

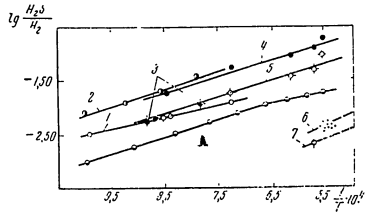

Fig. 171. Effect of temperature upon the equilibrium composition of the gaseous phase (H_2, H_2S) at varying contents of sulfur in metal as per different authors' data:

1 - FeS /3/; 2 - FeS /28/; 3 - 28.9% S /30/; 4 - 36.48% S /30/; 5 - 30% S /30/; 6 - /26/; 7 - 1% S /30/

Legend: A) Thermodynamic calculation.

As regards the relationship to alloy composition, it appeared, according to these data /30/, moreover that the ideal law of mass action is operative when sulfur contents does not exceed 4%,

$$\lg K = \lg \frac{p_{H_2S}}{p_{H_2}} \cdot \frac{N_{Fe}}{N_{FeS}} = -\frac{3025}{T} + 0{,}766. \qquad \text{(VIII, 74)}$$

The above relationship is more correct than the one suggested earlier /26/

$$\lg K = -\frac{4500}{T} + 1{,}853. \qquad \text{(VIII, 75)}$$

Finally, it was established /30/ that both for solid and liquid Fe-S alloys the isotherms reveal a horizontal section over an interval from 6 to 24% S (fig. 172).

In more recent works special measures were taken to eliminate thermal diffusion. Thus, in the case of induction furnaces, special gas heaters were used with argon being introduced into gas /31/. In other investigations /32/ hermetically sealed furnaces were utilized with spiral carbon heaters assuring a sufficiently even temperature field. In addition to this, the gas mixture was sparged through metal.

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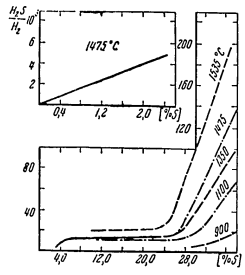

Fig. 172. Effect of temperature and sulfur contents on the equilibrium composition of the gaseous phase in Fe,S-H_2-H_2S systems.

Let us dwell for a while on the experimental data [31] pertaining to the temperatures 1530, 1610, and 1725°C and the sulfur contents ranging from 0.4 to 4.8%.

Minor corrections for thermal dissociation of hydrogen sulphide were usually introduced here into the initial compositions of the gaseous phase as per equation

$$\lg \frac{p_{H_2S}}{p_{H_2} p_{S_2}^{1/2}} = \frac{4740}{T} - 2{,}582. \qquad \text{(VIII, 76)}$$

Thereafter, a quantity similar to the equilibrium constant of reaction (VIII, 71) was calculated

$$K_1' = \frac{p_{H_2S}}{p_{H_2}[\%\,S]}. \qquad \text{(VIII, 77)}$$

Graphs were then plotted of $\lg K_1'$ against $\frac{1}{T}$ at [%S] = const. The values of K_1' were thereupon determined by interpolation for 1600°C, on the basis of which the isotherm recorded in fig. 173 was plotted. The straight-line relationship between $\frac{p_{H_2S}}{p_{H_2}}$ and [% S] was maintained approximately up to 0.6 - 0.8% A. Deviations therefrom indicate that the activity of sulfur

in the melt is not equal to its concentration, i.e., that this solution is imperfect.

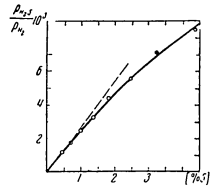

Fig. 173. Equilibrium composition of the gaseous phase in system Fe,S - H_2 - H_2S versus sulfur contents in melt (1600°C).

Therefore, the expression for the equilibrium constant should assume the following aspect

$$K_1 = \frac{p_{H_2S}}{p_{H_2} a_S} = \frac{p_{H_2S}}{p_{H_2}[\%\,S]} \cdot \frac{1}{\gamma_S} = K_1' \frac{1}{\gamma_S}, \qquad \text{(VIII, 78)}$$

whereupon

$$\lg \gamma_S = \lg K_1' - \lg K_1. \qquad \text{(VIII, 79)}$$

The dependence of the activity coefficient of sulfur γ_S upon its concentration can be determined, for instance, by means of extrapolation of the K_1' values with respect to the point where [%S] = 0. Since $\gamma_S = 1$ here, $K_1' = K_1$ according to equation (VIII, 78). Knowing the value of K_1' and K_1 for any contents of sulfur, it is possible to determine γ_S which corresponds to the given [%S].

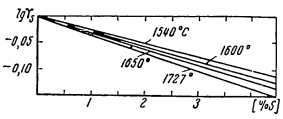

Fig. 174. Effect of temperature and the concentration of sulfur on its activity coefficient.

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In other words, γ_S represents the relationship of the tangent at any given point of isotherm $\frac{p_{H_2S}}{p_{H_2}}$, (%S) to its value for (%S) = 0, whence

$$\lg \gamma_S = \lg \operatorname{tg} \alpha - \lg \operatorname{tg} \alpha_0. \qquad \text{(VIII, 80)}$$

The values of γ_S for various [%S] and T determined in this manner are recorded in fig. 174. As to the temperature dependence of the equilibrium constant K_1 (fig. 175) of reaction (VIII, 71), and the variation of standard free energy ΔF°_S, according to these data, their aspect is as follows

$$\lg K_1 = -\frac{2150}{T} - 1{,}429, \qquad \text{(VIII, 81)}$$

$$\Delta F^\circ_{S,\,6} = 9840 + 6{,}54\,T. \qquad \text{(VIII, 82)}$$

Whereupon, for the process

$$\frac{1}{2} S_{2\,(gas)} = S_{(Fe)}, \qquad \text{(VIII, 83)}$$

upon utilization of equation (VIII, 76) for hydrogen sulfide dissociation, we obtain

$$\Delta F^\circ_{S,\,6} = -31\,520 + 5{,}27T. \qquad \text{(VIII, 84)}$$

It differs considerably from the equations derived on the basis of investigations conducted without elimination of thermal diffusion [29], [26]

$$\Delta F^\circ_{S,\,6} = -42\,526 + 11{,}01\,T, \qquad \text{(VIII, 85)}$$

$$\Delta F^\circ_{S,\,6} = -42410 + 10{,}35\,T. \qquad \text{(VIII, 86)}$$

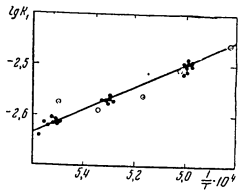

Fig. 175. Temperature dependence of the equilibrium constant for reaction (VIII, 71).

Thus, experiments conducted with greater precision reveal that the influence of temperature on the distribution of sulfur between metal and gas is smaller (formula VIII, 84), than it was previously thought [formulas (VIII, 85) and (VIII, 86)].

Reaction with Sulfurous Gas.

In the oxidizing atmosphere of an open-hearth furnace sulfur is to be found almost entirely in the form of SO_2. In view of this fact certain investigators [33], [34] were inclined to place the responsibility for the transfer of sulfur from gas to metal on reaction

$$S_{(Fe)} + O_{2\,(gas)} = SO_{2\,(gas)}. \qquad \text{(VIII, 87)}$$

However, this is not so. Actually, by combining equation (VIII, 84) with a similar expression

$$\Delta F_S = -86\,380 + 17{,}30\,T \qquad \text{(VIII, 88)}$$

for the reaction

$$\frac{1}{2} S_{2\,(gas)} + O_{2\,(gas)} = SO_{2\,(gas)}, \qquad \text{(VIII, 89)}$$

we find

$$\Delta F^\circ_{S,\,87} = -54\,860 + 12{,}03\,T, \qquad \text{(VIII, 90)}$$

whereupon

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$$\lg K_{S,\,87} = \lg \frac{p_{SO_2}}{p_{O_2} a_S} = \frac{11\,991}{T} - 2{,}63. \qquad \text{(VIII, 91)}$$

Calculations made with the aid of equation (VIII, 91) disclosed that the equilibrium constant $K_{S,87}$ for reaction (VIII, 87) is great at all temperatures important for metallurgists. It drops with rising temperature, but even at 2000°K it amounts to $10^{3.365}$. This points out to the considerable disinclination of sulfur to pass from SO_2 into metal according to reaction (VIII, 87).

Moreover, as emphasized by Karnaukhov [357], the presence of oxygen in the atmosphere causes oxidation of sulfides and a transfer of sulfur from metal to gas in the form of SO_2, i.e., a flow of reaction (VIII, 87) from left to right. In the presence of slag, there develops in it a reaction between the anions of sulfur (sulfides) and the cations of trivalent iron

$$S^{2-}_{(sl)} + 6\,Fe^{3+}_{(sl)} + 2\,O^{2-}_{(sl)} \rightarrow 6\,Fe^{2+}_{(sl)} + SO_{2\,(gas)}, \qquad \text{(VIII, 92)}$$

which also leads to the removal of sulfur in the form of SO_2.

A substantial role (see [367]) in combining sulfur with metal is played by another reaction, namely that of SO_2 dissolution

$$S_{(Fe)} + 2\,O_{(Fe)} = SO_{2\,(gas)}. \qquad \text{(VIII, 93)}$$

It was stated in chapter VII that the interaction of SO_2 with copper proceeds through dissociation of sulfurous gas at the interface into atoms with their subsequent dissolution in metal. The development of reaction (VIII, 93) from right to left is confirmed here by the validity of the cube root law

$$[\%\,S] = K \sqrt[3]{p_{SO_2}}.$$

With regard to SO_2 interaction with iron, the change of the standard free energy and the equilibrium constant for reaction (VIII, 93) may be determined by combining equation (VIII, 90) with an analogous equation for the solution of oxygen in iron [377]

$$O_{2\,(gas)} = 2O_{(Fe)}, \qquad \text{(VIII, 94)}$$

$$\Delta F^\circ_{O,94} = -55\,860 - 1{,}14T. \qquad \text{(VIII, 95)}$$

This gives

$$\Delta F_{S,\,93} = 1000 + 13{,}17T, \qquad \text{(VIII, 96)}$$

$$\lg K_{S,\,93} = \lg \frac{p_{SO_2}}{a_S a_O^2} = -\frac{218}{T} - 2{,}88. \qquad \text{(VIII, 97)}$$

It follows from equation (VIII, 97) that the equilibrium constant of reaction (VIII, 93) is a small quantity which depends little on temperature. This fact points to a relatively powerful solvent action of iron with regard to SO_2 which can be ascertained, for example, from the following activity values of sulfur and oxygen for reaction (VIII, 93) at 1800°K ($K'_{S,93} \approx 0.001$), determined in the assumption that

$$a_S = a_O$$

p_{SO_2}, atm	1,0	0,1	0,01
$a_S = a_O$	31,6	10,0	3,16

Thus, in the case under consideration the equilibrium conditions are favorable for the absorption of sulfur by metal from SO_2. This conclusion is borne out by the increased sulfur contents in steel smelted with sulfurous fuel.

In conclusion, a few words concerning the rate of iron interaction with gases containing sulfur. The number of investigations confined to this matter is scarce. Let us review the results obtained by Karamzin [387] who studied the kinetics of sulfur absorption by solid iron from an atmosphere of SO_2 and H_2S at 800-1000°C.

It transpired that the rate of the process in dealing with H_2S, is approximately twice as high as in the case of SO_2. In the latter instance, there forms apparently a compact blanket of $FeO \cdot FeS$, through which diffusion proceeds slower than through a layer of FeS (see part I of the present monograph, page 406).

Further, according to Karamsin, the absorption rate of the sulfur bearing gases grows in direct proportion to their partial pressures. This accords with the assumption concerning the great significance of the diffusion processes during the period of charge smelting. It should finally be noted that the rate of the process develops sharply upon reaching the melting point of the oxide-sulfide scale and the partial exposure of the metal. In seems that in these conditions, before the formation of a protective slag layer while the scale is molten, the most intensive absorption of sulfur by metal takes place.

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Effect of Elements Dissolved in Iron.

The introduction of carbon into metal is known to cause a decrease of sulfur solubility in it. In particular, Karamsin [39] provides a few data [4] according to which carbonization of iron increases the ratio of sulfur contents in slag to that in metal, i.e., (% S) : [% S], approximately by 4 - 5 times (see also [41]).

Silicon and partially phosphorus also reduce the solubility of sulfur in iron. Certain authors [42] believe that impurities can be broken down into three groups in accordance with the character of their action.

To the first of these belong the elements whose affinity with sulfur is less than that of iron. These substances, in their opinion, do not produce any substantial influence on the solubility of sulfur in iron. They refer Cu, Co, Ni, W, and others to this group of impurities. It should be noted, however, that the dissociation pressure of Cu_2S at high temperatures becomes noticeably lower than that of FeS, while at temperatures upwards of 1350°C it is lower even than that of MnS.

The second group incorporates the metals producing sulfides more stable than FeS. They reduce sulfur solubility. Classified here are Mn, Al, Cr, Ti, Zr, etc.

Finally, the third group includes elements which interact powerfully with iron forming with it various compounds. According to the authors of this classification, their addition reduces the concentration of "free" iron, causing thereby a drop in sulfur solubility. This group covers Si, C, and P.

Suggestions were even made [43] in this connection for the computation of sulfur activity in the presence of Si, C, and P, according to formula

$$a_S = \frac{1}{[Fe^*]} \cdot [\%\ S], \qquad \text{(VIII, 98)}$$

in which [Fe*] is the concentration of "free" iron.

Carbon and Silicon.

The effect of Si and C on the activity of S was experimentally studied also by way of equilibrium investigation of metal with gas, containing H_2 and H_2S. It turned out [44], in particular, for carbon-saturated iron that the activity of sulfur is double that registered in pure metal. As to other carbon concentrations, corresponding experimental data [45] may be found in fig. 176. It provides plots for S concentration versus C contents for a number of temperatures and compositions of the gaseous phase.

Knowing these relationships and the value of K_1 (see equation VIII, 78) it is easy to find the activity coefficients of γ_S for various carbon concentrations. The relationship between γ_S and N_S are shown in fig. 177.

Moreover, a melt containing 1% S and 99% Fe was taken for the standard state of sulfur in which $a_S = N_S$. The curve plotted in fig. 177 shows the growth of the sulfur activity coefficient with increasing carbon contents. A second curve is incorporated therein which illustrates an analogous influence of silicon [32].

Similar results were obtained by other authors [46], whose data are recorded in fig. 178. In this case γ_S refers to the binary system Fe - S, while γ_S refers to a ternary system, i.e., to Fe-C-S, or Fe-Si-S alloys. In full harmony with the curves in fig. 177, the addition of silicon increases γ_S more powerfully than the introduction of carbon, if the composition is recorded in atom %.

As to the influence of sulfur concentration, its growth leads to a drop of the activity coefficient of S both in the presence and in the absence of C and Si.

The attempts to provide a theoretical explanation for the action of carbon and silicon additions can be broken down into two groups. One of them considers the bonding of iron by additions to constitute the main cause, the second holds it to be due to the reduction of the number of vacant sites.

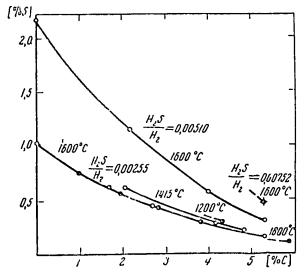

Fig. 176. Effect of temperature, gaseous phase composition, and the contents of carbon in its alloy with iron upon the concentration of sulfur in the latter.

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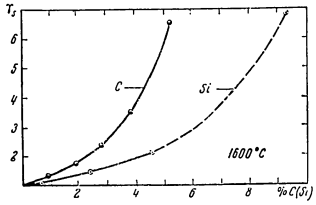

Fig. 177. Effect of silicon and carbon concentrations on the activity coefficient of sulfur in their alloys with iron.

To the extent that in low carbon concentrations each atomic percent of carbon increases γ_S approximately by 6%, a purely chemical interpretation must assume that iron combines with the admixture into a Fe_6C compound. Similar and highly improbable formulas of chemical compounds must be conjectured also for silicon [47].

More realistic, it seems, is the other version which may be reduced to the following [48]. Carbon has a greater affinity with iron than sulfur. The atoms of the latter are, therefore, being driven off by carbon from the environment of iron. From the ratio of C and Fe radii, it follows that each C atom can be surrounded by six atoms of Fe. This means that its appearance in the melt reduces approximately by 6 the number of the possible vacancies to be occupied by sulfur. To put it in another way, each atomic percent of carbon decreases the equilibrium contents of sulfur by 6%, approximately.

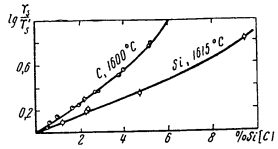

Fig. 178. Effect of silicon and carbon on the activity coefficient of sulfur in their alloys with iron.

The second interpretation departs from the fact that the number of vacant sites to be occupied by sulfur and carbon is always equal to one quarter of the total number of iron atoms (see chapter VII, page 428).

Assuming further that carbon and sulfur distribute themselves on an equal basis among the available sites, one finds

$$\gamma_S = \frac{1}{1-5(N_C+N_S)} \cdot \qquad \text{(VIII, 99)}$$

As may be seen from table 23, the above equation is in satisfactory agreement with the experimental data [32], at least up to 3% C.

Table 23. Comparison of the observed γ_S values in Fe - C - S alloys at 1600°C with those calculated according to formula (VIII, 99).

$\frac{p_{H_2S}}{p_{H_2}} \cdot 10^3$	Contents in the alloy, %		γ_S	
	C	S	Experiment	Calculation
2,44	1,70	0,59	1,75	1,73
2,42	2,75	0,42	2,57	2,57
2,43	0,01	0,97	~1	~1
2,46	2,82	0,41	2,62	2,62
2,49	0,98	0,73	1,42	1,39
2,52	1,97	0,55	1,97	1,89
2,55	3,84	0,29	4,00	5,12
4,93	2,20	1,10	1,95	2,03
5,12	4,02	0,57	4,20	0,95

Yet, the assumption of the equivalency of sulfur and carbon can hardly be substantiated. Neither the particle sizes, nor the mode of the existence of these elements in metal, or their affinity with iron — nothing seems to provide any grounds for such an assumption. If the non-equivalency of carbon and oxyten — consisting in that the first dissolves by way of replacement, whereas the other by way of intrusion [50] — is to be considered true, then this should be even more so with respect to sulfur and carbon inasmuch as the size of the S atom is larger than that of the O atom.

Furthermore, to the extent that the same basis of equality is acknowledged for the distribution of C and Si [51], one should expect a similar influence of Si and C admixtures upon the activity coefficient of sulfur. Experiments, however, do not support this theory.

As it transpires from figs. 177 and 178, after conversion into atomic percents, γ_S grows faster upon silicon introduction than after the addition of carbon.

Finally, it follows directly from the proposed explanation that the sum total of carbon and sulfur atomic fractions in saturated solutions should be equal to one fifth, i.e., $N_C + N_S = 0.2$. This rule is obeyed [52] only in a few cases, but by far not always.

The temperature and the composition of the gaseous phase affect the

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total concentration of sulfur and carbon. Thus, for examples, with the partial pressure ratio of H_2 and H_2S ($p_{H_2S} : p_{H_2} = 2.5$) being constant, the S and C contents varied with temperature in the following manner [32]: at 1200°C there was 4.35% C and 0.27% S in metal, whereas at 1600°C - 5.3% C and 0.16% S. At 1600°C and at the same concentration of carbon (5.30% C - saturated solution) the sulfur contents in iron increases from 0.16 to 0.48% together with growing $p_{H_2S} : p_{H_2}$ from $2.63 \cdot 10^{-3}$ to $7.52 \cdot 10^{-3}$.

Thus, a correct interpretation of the effect of C and Si on the contents of S in iron must be based on the non-equivalency of the sulfur and admixture atoms both with regard to their affinity with Fe, and in respect of their location in the solution.

Copper.

A study of the effect of copper admixtures on the activity of sulfur in iron was conducted at a temperature of 1550°C in Al_2O_3 (99%) crucibles which contained practically no silica at all [53]. The results obtained are recorded in fig. 179, from which it may be seen that introduction of Cu reduces a_S greater, the greater the contents of copper in the melt.

In explaining the results produced, the authors [53] proceed from the assumption that the bond of sulfur with copper is stronger than with iron. Hence, the introduction of copper into the melt forces the sulfur atoms to accumulate round copper atoms. The interaction energy of sulfur with the melt increases, while its activity declines.

The following considerations are set forth in support of the surmise concerning the greater bond of sulfur with iron. Since Fe - Cu and Fe - FeS binary alloys are prone to separate into two immiscible liquids, one may assume that there appear in them isolated groups which, in the first instance, are composed of copper, and in the second case, of FeS.

In the ternary system Fe - Cu - S, where copper atoms attract the atoms of sulfur and form stable bonds, these two types of groups unite with each other. At the same time the tendency to isolation, and consequently also to separation, augments.

Indeed, the fusibility diagram of the Fe-Cu-S system is characteristic for its extended region of separation into two liquids, one of which is rich in copper and sulfur, while the other manifests a high concentration of iron.

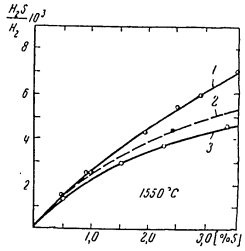

Fig. 179. Equilibrium composition of gas in H_2-S-Fe-Cu system versus concentration of copper and sulfur in alloy:

1 - Fe-S alloy; 2 - Fe-Cu-S alloy with Cu:S $\cong$ 1.3; 3 - same with Cu:S $\cong$ 4.0

INTERACTION OF METAL WITH SLAG.

As mentioned earlier, the furnace gases which contain sulfur are responsible for its transfer into metal. For this reason, exposed metal is gradually being enriched by sulfur. Slags capable of extracting sulfur are ordinarily used to decrease its contents in metal. A distribution of sulfur occurs thereby between two immiscible phases in conformity with Shilov's law. It is natural that the effect of sulfur elimination becomes a function of the temperature and the composition of metal and slag.

It has been long since established that successful removal of sulfur from metal into slag can be achieved through the use of highly basic slags rich in calcium oxide. An assumption was made in this connection [54] to the effect that desulfurization follows the reaction

$$FeS_{(met)} + CaO_{(sl)} = CaS_{(sl)} + FeO_{(sl)}. \qquad \text{(VIII, 100)}$$

It was initially believed that liquid slag does not deviate too much from ideal solution. While considering the metal phase as a dilute solution of FeS in Fe, it was customary to express the equilibrium constant for reaction (VIII, 100) not through activities, but through concentrations of reagents.

Thus, for instance, for slags rich in CaO and containing a small proportion of FeO and CaS, its expression was recorded [26] in the following aspect

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$$K_S = \frac{N_{CaS} N_{FeO}}{N_{CaO}\,|\%\ FeS|}, \qquad \text{(VIII, 101)}$$

where N_i = mole fractions of the corresponding components.

It appeared thereby that the temperature dependence can be satisfactorily described by equation

$$\lg K'_S = -\frac{2047}{T} - 0{,}337. \qquad \text{(VIII, 102)}$$

By a similar method, for reactions

$$FeS_{(met)} + MnO_{(sl)} = FeO_{(sl)} + MnS_{(sl)}, \qquad \text{(VIII, 103)}$$

$$FeS_{(met)} + MgO_{(sl)} = FeO_{(sl)} + MgS_{(sl)}, \qquad \text{(VIII, 104)}$$

the following equations were obtained

$$\lg K''_S = \lg \frac{N_{MnS} N_{FeO}}{N_{MnO}\,|\%\ FeS|} = \frac{4234}{T} - 0{,}271. \qquad \text{(VIII, 105)}$$

$$\lg K'''_S = \lg \frac{N_{MgS} N_{FeO}}{N_{MgO}\,|\%\ FeS|} = -\frac{7530}{T} - 0{,}337. \qquad \text{(VIII, 106)}$$

It followed from these that at 1600°C, $K'_S = 3.7 \cdot 10^{-2}$; $K''_S = 2.9 \cdot 10^{-3}$; $K'''_S = 4.6 \cdot 10^{-5}$, i.e., that the desulfurizing effect of MnO, and even more so in the case of MgO, is small in comparison with the effect produced by CaO.

However, with the development of the molecular theory of slags, it became common practice to introduce molar fractions of "free" lime into the expression for equilibrium constant K'_S instead of total CaO concentrations. The methods used to calculate this quantity varied depending on the character of the assumed compounds and the degree of their dissociation.

In basic slags, in particular, the presence of almost undissociated molecules $2CaO \cdot SiO_2$ and $3CaO \cdot P_2O_5$ was presumed to be possible.

Then

$$N_{CaO\,(free)} = N_{CaO} + N_{MgO} + N_{MnO} - 2N_{SiO} - 3N_{P_2O_5}. \qquad \text{(VIII, 107)}$$

Yet, the processing of the experimental data of a number of investigators with the aid of these equations, according to Samarin, Schwartzmann and Temkin [18], produced highly fluctuating and sharply divergent values K'_S. In this connection attempts were made to find other chemical compounds for which calculations could assure the constancy of K_S.

Thus, for example, in order to review the results of 212 experiments it became necessary to assume the existence [55] of the following molecules: $(2CaO \cdot SiO_2)_2$; $(CaO \cdot SiO_2)_2$; $4CaO \cdot P_2O_5$; $CaO \cdot Fe_2O_3$; $4CaO \cdot P_2O_5 \cdot CaF_2$; $2CaO \cdot Al_2O_3$. The presence of such molecules in liquid slag demands special proofs. Moreover, in crystal chemistry the dimers of calcium ortho- and metasilicates are totally unknown. On the contrary, the structure of these bodies (isolated SiO_4^{4-} tetrahedra and endless chains of them) would not permit for polymerication to occur without a change of composition.

Without dwelling any longer on similar attempts, we shall remark that a strong impulse towards the solution of the problem of sulfur equilibrium was given through the application of the ionic theory of slags. As is well known, equilibrium in a heterogeneous system (independently from the forms of its components' existence in different phases) demands compliance both with the law of mass action and with Shilov's law of distribution.

Consequently, alongside with the equation for the equilibrium constant of the reaction of desulfurization

$$K_S = \frac{a_{CaS}\, a_{FeO,\,Fe}}{a_{FeS,\,Fe}\, a_{CaO}}, \qquad \text{(VIII, 108)}$$

valid also are the expressions

$$I_S = \frac{a_{FeS}}{a_{FeS,\,Fe}}; \quad I_O = \frac{a_{FeO}}{a_{FeO,\,Fe}}. \qquad \text{(VIII, 109)}$$

In passing over to the ionic form

$$a_{CaS} = a_{Ca^{2+}} \cdot a_{S^{2-}}; \quad a_{CaO} = a_{Ca^{2+}} \cdot a_{O^{2-}}$$
$$a_{FeS} = a_{Fe^{2+}} \cdot a_{S^{2-}}; \quad a_{FeO} = a_{Fe^{2+}} \cdot a_{O^{2-}}$$

and upon replacement of the activities of FeS and FeO in the metal phase, in view of the smallness of their concentrations, by weight percentage of S and O, we obtain

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$$L_S = \frac{a_{Fe^{2+}} \cdot a_{S^{2-}}}{|\% S|}, \qquad \text{(VIII, 110)}$$

$$L_O = \frac{a_{Fe^{2+}} \cdot a_{O^{2-}}}{|\% O|}, \qquad \text{(VIII, 111)}$$

$$K_S = \frac{a_{S^{2-}} \cdot |\% O|}{a_{O^{2-}} \cdot [\% S]}. \qquad \text{(VIII, 112)}$$

On the basis of the theory of perfect ionic solutions, Samarin, Schwartzmann, and Temkin /18/ assumed the activities to be equal to ionic fractions in these equations, inferring that

$$a_{S^{2-}} = \frac{n_{S^{2-}}}{\Sigma n_-}; \quad a_{O^{2-}} = \frac{n_{O^{2-}}}{\Sigma n_-}, \qquad \text{(VIII, 113)}$$

where

$$n_{O^{2-}} = n_{FeO} \cdot n_{MgO} + n_{MnO} - 2\, n_{SiO_2}. \qquad \text{(VIII, 114)}$$

Then

$$K_S = \frac{L_S}{L_O} = \frac{n_{S^{2-}} |\% O|}{(n_{CaO} + n_{MgO} + n_{FeO} - 2\, n_{SiO_2}) |\% S|}. \qquad \text{(VIII, 115)}$$

Knowing from the analytical composition of the slag the number of moles n_1 of the corresponding components (CaO, CaS, MgO, FeO, SiO_2) and the weight percentage of S and O in metal at the moment when these two phases were in equilibrium, they computed the values of K_S. It transpired that the latter remain more or less constant so long as the silica contents in slag does not exceed 20-25%. On the other hand, the values of L_S and L_O, calculated in the same manner, begin to change appreciably at substantially smaller concentrations of SiO_2 (7-10%).

This was also established by Heinmann /56/ and other investigators /57/. As mentioned earlier (also see /2/), this fact is due to the acceptance of the hypothesis of the equivalence of all the ions of the same sign, i.e., a consequence of the premises based on the theory of perfect solutions. Upon the appearance in the melt of noticeable concentrations of silicon or aluminum-oxides and other complex anions this assumption, obviously, loses its validity.

In addition to the ionic fractions, it becomes necessary to introduce

into the expressions for K_S, L_S and L_O also the coefficients of activity $\gamma_{S^{2-}}$ and $\gamma_{O^{2-}}$ which indicate the degree of deviation of the real slag from perfect ionic solution. Then

$$L_S = \frac{N_{Fe^{2+}} \cdot N_{S^{2-}} \cdot \gamma_{Fe^{2+}} \cdot \gamma_{S^{2-}}}{|\% S|}. \qquad \text{(VIII, 116)}$$

$$L_O = \frac{N_{Fe^{2+}} \cdot N_{O^{2-}} \cdot \gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}}}{|\% O|}, \qquad \text{(VIII, 117)}$$

$$K_S = \frac{N_{S^{2-}} \cdot \gamma_{S^{2-}} \cdot |\% O|}{N_{O^{2-}} \cdot \gamma_{O^{2-}} \cdot |\% S|}. \qquad \text{(VIII, 118)}$$

At the same time the quantity $\gamma^2_{FeO} = \gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}}$ may be, for example, determined from one of the previously recorded empirical equations (see chapter V, page 339), in particular, on the basis of the formula proposed by Samarin and Schwartzmann /58/

$$\lg \gamma_{O^{2-}} = 1{,}53\, N_{SiO_4^{4-}} - 0{,}17. \qquad \text{(VIII, 119)}$$

As may be seen from fig. 180, this relationship remains valid also when instead of $N_{SiO_4^{4-}}$ the sum is taken of the ionic fractions of all complex anions (SiO_4^{4-}, PO_4^{3-}, AlO_3^{3-}) and when CaO is replaced by MnO, i.e., in non-calcareous slags.

As concerns $\gamma^2_{FeS} = \gamma_{Fe^{2+}} \cdot \gamma_{S^{2-}}$, bearing in mind the considerable constance of K_S, it is possible to assume that γ_{FeS} does not differ very much from γ_{FeO}. Then the variations of γ^2_{FeS} with SiO_2 may, in the first approximation, be encompassed by the same empirical equation, in particular, by expression (VIII, 119).

It should be borne in mind, however, that the applicability of all these empirical corrections must be limited by 30% contents of SiO_2 ($N_{SiO_4^{4-}} \cong 0.9$), since the changeover to acid slags is accompanied by the formation of other, more complex anions, whose influence is apparently far more difficult to evaluate.

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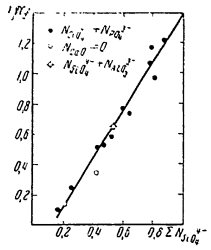

Fig. 180. Dependence of the activity coefficient of the oxygen anion ($\gamma_{O^{2-}}$) on the aggregate contents of complex anions ($\sum N_{SiO_4^{4-}} = N_{SiO_4^{4-}} + N_{PO_4^{3-}} + N_{AlO_3^{3-}}$)

Let it be mentioned in conclusion that the considerable absolute values of γ^2_{FeO} and γ^2_{FeS} have induced certain authors to assume the existence in liquid slags of molecules of oxides and of their compounds. The considerations exposed in Chapter V seem to indicate that this fact speaks rather in favor of a sharply expressed micro-inhomogeneity of such melts, and of the existence in them of cybotactic regions enriched by various sorts of ion pairs.

Upon these general remarks, it appears to be opportune to pass over to a detailed description of the influences produced by the phase compositions and temperature upon the processes of desulfurization.

INFLUENCE OF SLAG BASICITY

Of the four basic oxides CaO, MgO, FeO, and MnO, which are most commonly found in slags, it is important to single out FeO to be subsequently more carefully analyzed, since only FeO and FeS are noticeably soluble in iron.

By way of a quantitative characteristic of the process, let us take the ratio of sulfur concentrations in slag and in metal

$$L'_S = \frac{(S)}{[\%\ S]} \qquad \text{(VIII, 120)}$$

and call it the index of desulfurization. Since the contents of sulfur in slag is, ordinarily, small, its weight and atomic concentrations are in direct proportion to each other.

In view of this fact, the index under consideration may be represented according to the ionic theory by the expression

$$L'_S \sim \frac{N_{S^{2-}}}{[\%\ S]} = L_S \frac{1}{N_{Fe^{2+}} \cdot \gamma_{Fe^{2+}} \cdot \gamma_{S^{2-}}}. \qquad \text{(VIII, 121)}$$

If the concentration of Fe^{2+} in slag and the temperature are given, then L'_S will depend mainly on the product of the activity coefficients of iron and sulfur ions. The desulfurization index turns out to be inversely proportional to this product

$$L'_S \sim \frac{\text{const}}{\gamma_{Fe^{2+}} \cdot \gamma_{S^{2-}}} = \frac{\text{const}}{\gamma^2_{FeS}}. \qquad \text{(VIII, 122)}$$

As indicated earlier, the increase of the contents of SiO_2 and other substances (P_2O_5, Al_2O_3, and so on) which yield complex anions, augments substantially γ_{FeS} [see, for instance, equation (VIII, 119)]. On the other hand, the growth of the concentration of bases, for instance CaO, must decrease γ_{FeS} strongly, i.e., increasing the desulfurization index.

Numerous tests are known to support the foregoing [59], [60], [61], [63], [64], [65], [66]. The data produced by Samarin and Teodorovich [67] in tests run in an arc furnace are recorded here by way of illustration. These results are represented in fig. 181, which shows that in spite of a considerable spread of points, there appears to be a clearcut parallelism here between the percentage of CaO and L'_S.

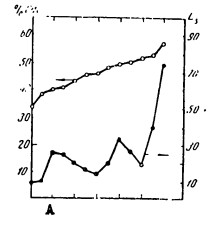

Fig. 181. Effect of calcium oxide contents in slag upon the desulfurization index L'_S.
A. - Fusion in the order of growth of N_{CaO}

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A similar relationship for a variety of temperatures (1550 and 1675°C) was obtained by other authors [65] in a high-frequency furnace with a rotating crucible and a device for hermetic sealing, which assured the runs being made in an atmosphere containing 85.5% N_2, 2.7% CO, 1.4% CO_2 and 0.4% O_2. In all test series in which the metal was either oxidized or reduced by silicon, or simultaneously carbonized, the growth of the desulfurization index was registered with waxing CaO concentration (see, for example, fig. 182).

Analogous observations pertaining to the effect of CaO upon [S] were also recorded by Pavlov [68] who made a survey of the production experience of one of our Southern metallurgical plants which used sulfurous coke. From fig. 183 it may be seen that the contents of sulfur in cast-iron falls regularly with the increase of slag basicity, or more precisely, of the $CaO-SiO_2$ ratio. In order to determine the effect of partial CaO replacement by other basic oxides (MgO, MnO, and so on), the index of sulfur distribution can be more conveniently calculated from expression (VIII, 118).

$$L'_S = \frac{(S)}{|\%S|} = K_S \frac{N_{O^{2-}}}{|\%\ O|} \cdot \frac{\gamma_{O^{2-}}}{\gamma_{S^{2-}}} \qquad \text{(VIII, 123)}$$

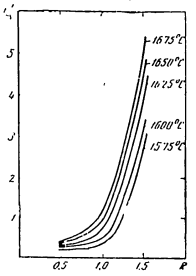

Fig. 182. Desulfurization index L_S versus the degree of slag basicity (R = CaO:SiO_2) and temperature, upon reduction through admixture of 0.2-05% of silicon.

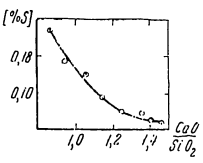

Fig. 183. Effect of slag basicity on the contents of sulfur in cast-iron.

If the percentage of oxygen in metal is given, while the concentration of O^{2-} anions is maintained constant, then the introduction of Mg^{2+} and Mn^{2+} cations instead of Ca^{2+} should affect only the relationship

of the activity coefficients. Inasmuch as the radii of the Mg^{2+}(0.78Å) and Mn^{2+}(0.91Å) ions are smaller than that of Ca^{2+}(1.06Å), their interaction energy with O^{2-} and S^{2-} anions is greater. The emergence of these cations in the melt will cause a decline of both activity coefficients.

Yet, since the size of the S^{2-} anion (1.74 Å) is greater than that of O^{2-} (1.32 Å), $\gamma_{O^{2-}}$ will decrease more than $\gamma_{S^{2-}}$. In other words, the replacement of MgO, or MnO, for CaO may produce a drop in L'_S.

It is difficult to say in advance how considerable this drop is. Should one judge it by analogy with the variation of $\gamma_{FeS} / \gamma_{FeO}$ ensuing upon the admixture of SiO_2, one might expect L'_S to be practically constant. On the contrary, should one proceed from equations (VIII, 102), (VIII, 105) and (VIII, 106), then one could assume that there is a possible drop of L'_S. Actually, by comparing expressions (VIII, 101) and (VIII, 118) we find that

$$K'_S = K_S \frac{N_{FeO}}{[\%\ O]} \cdot \frac{\gamma_{O^{2-}}}{\gamma_{S^{2-}}}. \qquad \text{(VIII, 124)}$$

When the percentages of FeO in slag and of oxygen in metal are fixed, the magnitude of K'_S depends only on the ratio of the activity coefficients. Since equations (VIII, 102), (VIII, 105) and (VIII, 106) produce sharply differing K'_S values, the ratio $\gamma_{O^{2-}} / \gamma_{S^{2-}}$ should be assumed to vary strongly with the change from CaO to MnO, and then to MgO.

However, the questionable accuracy of the cited equations does not lend confidence to the conclusion concerning the fall of K'_S and L'_S upon the replacement of Ca^{2+} cations by those of Mn^{2+} and Mg^{2+}. The available published material fails to produce unambiguous indications to this effect and speaks rather more in favor of a small variation of L'_S.

Thus, according to Rulla and Hess [69], MgO admixtures from 4 to 6.8% decrease L'_S. Further increase of MgO contents, though somewhat augmenting L'_S, still causes it to remain smaller than in the absence of MgO. However, it is true that in slags which contain 54% CaO, where SiO_2:CaO = = 0.45, L'_S also increases with growing MgO concentration. But the authors are inclined to ascribe this to the liquefying action of MgO, i.e., believing that these data do not pertain to the state of equilibrium.

Furthermore, according to Kochin [68], experimental runs with siderite containing highly magnesian gangue, revealed that a considerable decline in the desulfurizing capacity of slag is to be observed beginning with 18% MgO (see also [66]).

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Yet converse conclusions should also be registered. For example, Pavlov /68/ as well as Semik /70/ observe that a partial replacement of CaO by MgO does not affect desulfurization. The same transpires also from the results obtained by other authors /71/.

As a matter of fact, analysis /55/ of a great number of published data indicates that the index of sulfur distribution depends mainly on the basicity of slag R. The latter is understood to mean the difference between the aggregate molar concentrations of the basic (CaO, MgO, MnO) and acid (SiO_2, P_2O_5, Al_2O_3, Fe_2O_3) oxides. In this conjunction FeO and CaF_2 are often considered as neutral substances.

Fig. 184 shows a straight-line which illustrates the growth of L'_S with R for heats run with slags containing no MnO, while the points refer to tests in which the MnO percentage in slag varied from 16 to 39%. As may be seen from this diagram, the points are located close to the straight-line, i.e., the effect of MnO is equivalent to that of CaO and MgO.

Karmazin /38/, /39/ also believes that the desulfurization index is primarily determined by the basicity of slag R. To calculate the value of L he deems it possible to employ the following empirical expression

$$L'_S = \frac{(S)}{|\% S|} = 1{,}5 + 15R, \qquad \text{(VIII, 125)}$$

where

$$R = 0{,}0178\,(CaO) + 0{,}0141\,(MnO) + 0{,}025\,(MgO) - 0{,}333\,(SiO_2) - \\ - 0{,}0282\,(P_2O_5) - 0{,}0196\,(Al_2O_3) - 0{,}0062\,(Fe_2O_3). \qquad \text{(VIII, 126)}$$

In the last equation the concentrations of the components are given in percentages by weight. Formulas (VIII, 125) and (VIII, 126) are valid according to the author's data for the R's located within − 1.0 to + 1.6. They reflect the almost complete equivalence of the desulfurizing action of CaO, MgO, and MnO.

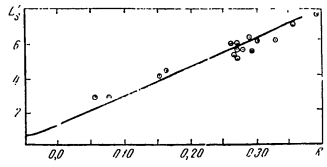

Fig. 184. Effect of manganous oxide (from 16-39% - points) on L'_S at different basicity of slag R
Solid line is the standard relating to the slags free from MnO.

It should be noted that the empirical relationship of L'_S versus R which is sometimes represented in the form /55/ of

$$L'_S = a + b\,|N_{CaO} + N_{MgO} + N_{MnO} - 2N_{SiO_2} - 4N_{P_2O_5} - N_{Fe_2O_3} - \\ - 2N_{Al_2O_3}| \simeq a + bR, \qquad \text{(VIII, 127)}$$

may, with certain allowances, as shown by Yessin, be produced from equation (VIII, 123).

Indeed, the ionic fraction of oxygen $N_{O^{2-}}$ in a sufficiently basic slag /18/ can be expressed by molar concentrations of the components

$$N_{O^{2-}} = N_{FeO} + N_{CaO} + N_{MgO} + N_{MnO} - 2N_{SiO_2} - \\ - 3N_{P_2O_5} - N_{Fe_2O_3} - N_{Al_2O_3} \cong N_{FeO} + R \qquad \text{(VIII, 128)}$$

approximately in the same way as R, particularly so, if the composition of the chemical compounds[1]) is assumed to be the same in both cases.

This is due to the fact that both contents values (R and $N_{O^{2-}}$) of basic oxides are recorded with the plus sign (sources of O^{2-} ions), whereas the concentrations of the acid oxides (bonding O^{2-} during the formation of anions) appear with the minus sign. Only the concentration of manganous oxide is added to the quantity R since it remained unaccounted for in the latter and because it also represents a source of oxygen ions.

In this manner, the following expression is derived from (VIII, 123)

$$L_S = K_S \frac{1}{|\%O|} \cdot \frac{\gamma_{O^{2-}}}{\gamma_{S^{2-}}} (N_{FeO} + R) \simeq a + bR, \qquad \text{(VIII, 129)}$$

which, like formula (VIII, 127), includes two augends, one of which contains R while the other does not.

As to the common variable factor

$$\frac{K_S}{|\%O|} \cdot \frac{\gamma_{O^{2-}}}{\gamma_{S^{2-}}},$$

it will be relatively constant only when the variation of the degree of

1) In equations (VIII, 127) and (VIII, 128) the chemical compound composition is different for the phosphates and the aluminates. In this case the statement remains valid if the contents of P_2O_5 and Al_2O_3 is small in slag.

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metal oxidation, ie.e, [30], is small, since the ratio $\gamma_{O^{2-}}/\gamma_{S^{2-}}$ in basic slags changes little with their composition.

Apart from this, one should also bear in mind that the addend $\underline{a}$ incorporates the ratio $\frac{N_{FeO}}{[30]}$ which can be considered as more or less constant for slags containing less than 10% of acid oxides. With the slag composition approaching that of orthosilicate, $N_{O^{2-}}$ will drop less rapidly than it follows from equation (VIII, 128) in view of the detachment of O^{2-} during the partial dissociation of the complex anions. In consequence thereof, quantity $\underline{a}$ will include still another augend increasing with the drop of basicity and partly compensating for the dimishing FeO/[30] ratio.

An attempt was made recently [72] to determine the ratio of a_{CaO}/a_{CaS} in slag on the basis of a study of the equilibrium

$$CaS_{(solid)} + H_2O_{(gas)} = CaO_{(solid)} + H_2S_{(gas)}, \qquad \text{(VIII, 130)}$$

for which it was established that

$$\Delta F^\circ = 15\,650 - 0{,}87T. \qquad \text{(VIII, 131)}$$

According to equation (VIII, 118) this relationship is equal to

$$\frac{a_{CaO}}{a_{CaS}} = \frac{a_{O^{2-}}}{a_{S^{2-}}} = K_S \frac{|\%S|}{|\%O|}.$$

With a given [30] it may serve as a measure of the desulfurizing power of slags.

In conjunction with other thermodynamic data it was disclosed that the ratio a_{CaS}/a_{CaO} augments with sulfur concentration in slag and falls with its growing basicity. The a_{CaS} calculated from these results varies with the contents of sulfur in slag according to the curve plotted in fig. 185.

At the same time the value of $a_{CaS} = 1$ corresponds approximately to calcium sulfide saturated slag.

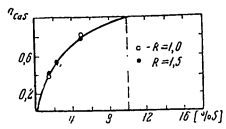

Fig. 185. Dependence of calcium sulfide activity in blast-furnace slags of varying basicity ($R = CaO:SiO_2$) upon sulfur concentration in them.

Let it be noted in conclusion that relatively recently various ways have been proposed for the treatment of liquid cast-irons by solid calcium oxide with the addition of coke fines in special rotary kilns [73]. It is supposed that the following reaction develops here

$$2S_{(Fe)} + Si_{(Fe)} \quad 2CaO_{(solid)} = 2CaS_{(solid)} + SiO_{2\,(solid)}, \qquad \text{(VIII, 132)}$$

as a result of which no liquid slag is formed, since calcium sulfide and silica are being absorbed by the surface layers of lump lime.

EFFECT OF FERROUS OXIDE.

Reference is repeatedly made in the literature to the effect that additions of ferrous oxide reduce considerably the index of desulfurization L_S^1 (see [60], [61], [62], [74] and others). According to the molecular hypothesis this fact is usually explained [63] by the inverse process of the homogeneous reaction in slag

$$FeS_{(sl)} + CaO_{(sl)} = FeO_{(sl)} + CaS_{(sl)} \qquad \text{(VIII, 133)}$$

due to increasing FeO concentration.

From the viewpoint of the ionic theory this reaction becomes senseless and changes into identity

$$S^{2-}_{(sl)} + O^{2-}_{(sl)} = O^{2-}_{(sl)} \quad S^{2-}_{(sl)}. \qquad \text{(VIII, 133')}$$

The reality of the (VIII, 133) process apparently can neither be substantiated by a reference to the micro-inhomogeneity of slags, i.e., to the existence in the melt of regions rich either in highly interacting Fe^{2+} and O^{2-} ions, or in more weakly combined Ca^{2+} and S^{2-} ions.

The fact of the matter is that Ol'shansky [75] had experimentally

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established a lowering of FeS solubility with the increase of CaO and Al_2O_3 contents in orthosilicate melts. The presence of MgO, on the other hand, was practically untraceable therein.

He attributes this to the fact that FeS, as a substance with a considerable share of metallic bonds, is contained in "ion-electron" regions which are rich in FeO. If the latter be partially substituted in silicate melts by CaO, then the volume of these regions would decrease with a consequent drop of FeS solubility. The absence of any effect upon admixture of MgO is due to the closeness of the Fe^{2+} and Mg^{2+} cation radii.

Thus it is hardly possible to speak of the existence of cybotactic groups with a predominant contents either of Fe^{2+} and O^{2-} ions, or Ca^{2+} and S^{2-} ions, at least as far as this concerns slags containing a sufficient quantity of silica.

Furthermore, had ferrous oxide been fully identical to the basic oxides specified earlier, its effect on L_S' would have been relatively as small as that resulting from the replacement of CaO by MgO. The effective action of FeO is related to the previously mentioned fact that only Fe^{2+} cations are capable of liquidating the continuous accumulation of charges arising during the passage of O^{2-} anions from slag into metal.

To put it differently, the increase of FeO contents, when the basicity (or Fe^{2+} at a given O^{2-} concentration) is fixed, augments the degree of steel oxidation, that is leads to the growth of /107. According to equation (VIII, 123) this results in a drop of the desulfurization index.

Analogous results may be obtained also upon application of expression (VIII, 121). The increase of $N_{Fe^{2+}}$ causes here a direct reduction of L_S', because the growth of the concentration of Fe^{2+} ions contributes to a greater transfer of S^{2-} from slag to metal.

The foregoing is illustrated by the data contained in table 24, which show /65/ that the desulfurization index L_S' diminishes with increasing oxidation of metal and declining $CaO:SiO_2$ ratio.

Table 24. Effect[1] of metal reduction upon the index of desulfurization L_S' at 1600°C

Oxidized iron			Iron reduced by silicon			Iron reduced by silicon and carbon		
$\frac{\%CaO}{\%SiO_2}$	L_S'	K	$\frac{\%CaO}{\%SiO_2}$	L_S'	K	$\frac{\%CaO}{\%SiO_2}$	L_S'	K
0,478	0,200	0,0705	0,381	0,227	0,0269	0,655	1,274	—
0,917	0,356	0,0380	0,953	0,437	0,0250	1,090	7,123	—
1,335	0,665	0,0287	1,257	2,043	0,0357	1,418	40,30	—
1,668	0,811	0,0310	1,584	3,680	0,0538	1,823	197,0	—

1) It should be borne in mind that the introduction of Si and C during reduction augments the activity coefficient of sulfur in metal which also contributes to an increase of L_S'.

Similar results are recorded by Samarin /76/, who indicates that L_S' amounts to 3-4 in oxidizing slags when the ratio of CaO to the sum of MnO + FeO is equal to 0.88, whereas for slags of the reduction period, when this ratio varies from 30 to 39, the index of desulfurization is considerably higher and attains 23 and even 49.

Various empirical formulas also speak in favor of a decrease of L_S' with growing FeO concentration in slag, for instance, /69/

$$L_S' = L'_{FeS} + K_{MnS}\frac{(MnO)}{(FeS)}, \qquad \text{(VIII, 134)}$$

or /61/

$$L_S' = \frac{(CaO)}{(FeO)K'_{1,S}} + \frac{(Mn)}{K_{2,S}}. \qquad \text{(VIII, 135)}$$

Similar relationships were also produced by Morozov, Agapov, and Pugachov.

A number of investigators, Karmazin /38/, /39/, for instance, and others /55/, believe, on the contrary, that FeO cannot be classified among the oxides which determine the basicity of slag. Ferrous oxide, in their mind, is a ballast diluent similar to CaF_2.

This conclusion is supported by a diagram (fig. 186) in which the plotted points represent the data relative to ferrous slag containing from 3.0 to 70% FeO. These points vary irregularly along the so-called standard

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line reflecting the relationship between L'_S and R. The location of the points pertaining to the slags with a varying percentage of calcium fluoride (from 4 to 17.6%) is similar.

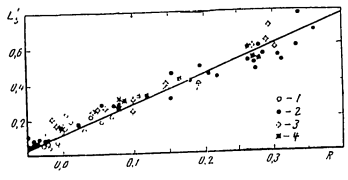

Fig. 186. Effect of FeO on L'_S at temperatures ranging from 1580 to 1650°C.

Solid line - standard. Points - experimental data referring to slags characterized by various concentrations ($\frac{\text{g-mol. FeO}}{100\ \text{g}}$):
1 - from 0.03 to 0.15; 2 - from 0.15 to 0.40; 3 - from 0.40 to 0.60; 4 - from 0.60 to 0.80.

Although these authors do not deny that L'_S drops with growing (FeO), they still are apt to interpret this drop erroneously as a result of a reduction of the slag basicity in consequence of partial replacement of CaO (or MgO and MnO) by FeO. They strive to replace the growth of the denominator (or more precisely of /40/) in equation (VIII, 123) by reducing the numerator ($N_{O^{2-}}$) disregarding the oxygen ion contributed by FeO.

The influence exerted by FeO on an equal basis with other oxides, which increases the O^{2-} anion contents in slags, can be traced, for example, from the equation advanced by Morozov, Agapov, and Pugachov

$$L'_S = 0{,}5 + 2{,}25[N_{FeO} + N_{CaO} + N_{MnO} + N_{MgO} - 2N_{SiO_2} - N_{Al_2O_3} - 3N_{P_2O_5}], \qquad \text{(VIII, 136)}$$

in which is included in the brackets the expression for $N_{O^{2-}}$, i.e., the quantity R which incorporates the mole fraction of ferrous oxide.

It seems that the experimental data embraced by relationship (VIII, 136) referred to metals oxidized approximately to the same degree (/40/ $\cong$ const). Only in such a case does the recorded relationship follow from equation (VIII, 123) upon consideration of the statement made previously with regard to the detachment of O^{2-} as a result of complex anion dissociation.

From the experimental data accumulated in Samarin's, Schwartzmann's and Temkin's work /18/ it transpires that sulfur can be eliminated from steel by almost pure ferrous oxide. Moreover, they showed that it is precisely in this case that the simplest law of distribution (relationship of the concentrations of substances and not of their activities) proves to be valid.

Indeed, if the slag should contain only FeO and a small proportion of FeS, the ionic fraction of Fe^{2+} would be equal to unity, while that of sulfur would coincide with the mole fraction of FeS. Then, pursuant to the theory of perfect solutions

$$L_{S,1} = \frac{N_{Fe^{2+}} \cdot N_{S^{2-}}}{|\%\ S|} = \frac{(FeS)}{|\%\ S|} = L'_S, \qquad \text{(VIII, 137)}$$

i.e., the index of desulfurization would appear to be directly proportional to the coefficient of distribution. In other words, the law of distribution would in this case assume the simplest form.

The same conclusion may be arrived at upon utilization of a more general expression (VIII, 123). In melts consisting almost entirely of pure FeO, the oxygen contents in metal is a function only of temperature, while $N_{O^{2-}} \cong 1$. Considering the generally small variation of the $\gamma_{O^{2-}} / \gamma_{S^{2-}}$ ratio changing composition, we find

$$L'_S = \frac{(S)}{|\%\ S|} = \text{const}, \qquad \text{(VIII, 138)}$$

and arrive at the same simple form of the law of distribution.

In conclusion let us mention that according to the observations of a number of authors, Danilov /77/ for one, the rate of desulfurization during the oxidizing period of an industrial heat increases with the growth of FeO contents in slag. This positive role played by ferrous oxide is negated by Karmazin /38/, who believes that it is not the iron oxides but the oxidizing atmosphere of the furnace that is responsible for the conspicuous development of the desulfurization process throughout this period of smelting.

EFFECT OF CALCIUM FLUORIDES AND CHLORIDES.

It has been long established (since 1892) in metallurgical practices that the addition of CaF_2 or $CaCl_2$ to slag reduces the percentage of sulfur in metal /60/. These observations are also confirmed by laboratory experiments. For example, Samarin and Teodorovich /67/ came to the conclusion on the basis of runs made in a laboratory arc furnace that the contents of sulfur in metal drops with increasing CaF_2 concentration.

For a certain period of time it was assumed that volatile fluorides of sulfur form in slag in the presence of CaF_2 /78/, /79/, /80/. Yet, this surmise is erroneous since fluorides of sulfur are absolutely unstable at elevated temperatures. Moreover, direct tests /81/ conducted in vacuo revealed that sulfur does not volatilize from slags containing CaF_2. In

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the presence of the latter, one could sooner expect a sublimation of SiF_4 to occur if the SiO_2 concentration is sufficient.

An explanation of the favorable influence of CaF_2 and $CaCl_2$ from the standpoint of the ionic theory was first advanced by Samarin, Schwartzmann and Temkin [18]. Introduction of CaF_2 or $CaCl_2$ does not affect the number of cations, but increases that of the anions, since instead of one O^{2-} (or S^{2-}) there appear $2F^-$ or $2Cl^-$. This actually leads to a decrease of $N_{S^{2-}}$ in view of the growth of the denominator of expression

$$N_{S^{2-}} = \frac{n_{S^{2-}}}{n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO} + 2n_{CaF_2}}. \qquad \text{(VIII, 139)}$$

Since in accordance with the theory of perfect ionic solutions

$$[\%\ S] = \frac{N_{Fe^{2+}} \cdot N_{S^{2-}}}{L_S}, \qquad \text{(VIII, 140)}$$

then the constancy of $N_{Fe^{2+}}$ and the drop of $N_{S^{2-}}$ are responsible for the decrease of the contents of sulfur in metal.

In confirmation of the foregoing, the authors produce the calculations of heats, the slags of which contained up to 30% CaF_2 and $CaCl_2$. Moreover, K_S computed on the basis of the theory of perfect ionic solutions turned out to be practically the same both in the case when CaF_2 and $CaCl_2$ (0.070-0.075) were present as well as in their absence (0.080).

The same deductions can be drawn also from the general equations (VIII, 121) and (VIII, 123). According to the first

$$[\%\ S] = \frac{N_{Fe^{2+}} \cdot N_{S^{2-}} \cdot \gamma^*_{FeS}}{L_S}. \qquad \text{(VIII, 141)}$$

The addition of CaF_2 or $CaCl_2$ reduces the concentrations not only of the simple (O^{2-}, S^{2-}), but also of the complex (SiO_4^{4-} and so on) anions. As has already been mentioned (see equation [VIII, 119]) this provokes[1] a drop of γ_{FeS} which together with the reduction of $N_{S^{2-}}$ leads to diminishing [%S].

1) The crux of the matter is that for the change γ_{FeO} essential is only the ratio of the simple and the complex anions, since the replacement of $2O^{2-}$ by $4E^-$, in contrast to SiO_4^{4-}, practically does not affect the energy of interaction.

It follows further from equation (VIII, 123) that

$$[\%\ S] = \frac{N_{S^{2-}} \cdot [\%\ O]}{N_{O^{2-}} \cdot K_S} \cdot \frac{\gamma_{S^{2-}}}{\gamma_{O^{2-}}}. \qquad \text{(VIII, 142)}$$

Here the ratio of $N_{S^{2-}}/N_{O^{2-}}$ remains constant because the addition of CaF_2 or $CaCl_2$ to slag changes only the denominator in the expressions for $N_{S^{2-}}$ [see equation (VIII, 139)] and $N_{O^{2-}}$. The latter is the same in both cases and can be reduced. As regards the $\gamma_{S^{2-}}/\gamma_{O^{2-}} \cong$ const, reference to this fact will be found above.

Thus the contents of sulfur in metal will be determined only by the magnitude of [%S] which should be falling in conformity with formula (VIII, 117) since $N_{O^{2-}}$, $N_{SiO_4^{4-}}$, and γ_{FeO} decrease with the growth of CaF_2 (or $CaCl_2$). Consequently the introduction of CaF_2 or $CaCl_2$ into slag causes a reduction of the equilibrium contents of sulfur in metal.

Let it be said in conclusion, that a number of authors are justified in stating that slag viscosity decreases as a result of CaF_2 and $CaCl_2$ additions [41], [60], [61]. This could accelerate the process of desulfurization, which generally speaking, develops at a comparatively slow pace [59], [69], [81], [82], etc.

EFFECT OF MANGANESE.

In a sense manganese occupies an intermediate position between iron and alkali-earth metals. Indeed, in contradistinction to the latter, it is infinitely soluble in liquid iron at high temperatures. However, its protoxide (MnO) and sulfide (MnS), like those of alkali-earth metals (CaO, MgO, CaS, MgS) and unlike FeO and FeS, are insoluble in molten iron.

These characteristics of manganese make it necessary to consider separately its influence on the process of desulfurization.

Being more electro-negative than iron, manganese combines with oxygen and sulfur in a more stable manner. For this reason its additions to iron containing sulfur reduce the activity coefficient of same. In this respect its action is similar to that of copper (see above).

Fig. 187 shows curves which illustrate [83] the effect of Si, C, P, Al, Cu, and Mn additions upon γ_S. A comparison of the curves reveals that the first four elements immobilize iron and thereby enhance the activity of sulfur. The last two (Cu and Mn), on the contrary, interact with sulfur more powerfully than iron and diminish γ_S.

Different authors diversely evaluate the role and the significance of

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manganese in the process of sulfur distribution between metal and slag. However, abundant factual material unambiguously confirms the beneficial effect of manganese, at least, for the purpose of cast-iron desulfurization.

Thus, for instance, Grum-Grzhimaylo /59/ records the data of Geyke /84/ who, by the hardening method, studied the effect of increasing manganese contents and dropping temperature upon the concentration of sulfur. As shown in fig. 188, both these circumstances facilitate desulfurization, a fact which Grum-Grzhimaylo explains by a shift of the reaction

$$FeS_{(met)} + Mn_{(met)} = MnS_{(met)} + Fe_{(met)} \qquad \text{(VIII, 143)}$$

to the right, inasmuch as it proceeds with heat liberation.

Similar results were obtained by a series of other authors /39/, /41/, /85/, /86/, /87/. Part of these data is recorded in fig. 189, from which it follows that the contents of sulfur diminishes sharply with the growth of manganese concentration, approximately up to 1%, whereupon a further increase of /Mn/ produces a weaker influence. In addition to this, the reduction of temperature from 1600 to 1200°C results in an effective removal of sulfur from cast-iron.

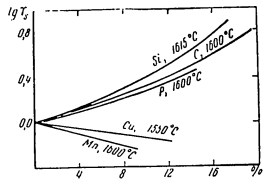

Fig. 187. Activity coefficient of sulfur in its alloy with iron and alloying admixtures versus concentrations of the latter.

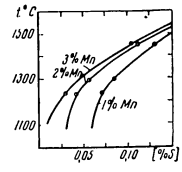

Fig. 188. Effect of the temperature and manganese concentration upon the contents of sulfur in cast-iron.

On the basis of the shapes of curves (see fig. 189) which resemble hyperbolas, Herty and other investigators /87/ proposed the equation

$$[\%\,S][\%\,Mn] = \text{const.} \qquad \text{(VIII, 144)}$$

The latter is usually considered to ensue from the formula of solubility product for low-solubility salt, while assuming the sulfide of manganese to be as such with respect to iron

$$N_S N_{Mn} \gamma_S \gamma_{Mn} = \Pi_{MnS}. \qquad \text{(VIII, 145)}$$

However, for the expression (VIII, 145) to be valid, it is necessary for pure MnS, instead of MnS dissolved in slag, to exist in the state of equilibrium with metal. To the extent that this does not usually seem to occur, equation (VIII, 144) cannot be substantiated on the basis of formula (VIII, 145).

Relationship (VIII, 144) bears an empirical character. This is also confirmed by the fact that, according to Karmazin /39/, another dependence in a number of cases proved to be more accurate, viz.:

$$[\%\,S] = \frac{0,04}{[\%\,Mn]} + 0,015. \qquad \text{(VIII, 146)}$$

From the point of view of the ionic theory, it is most essential in the interpretation of the effect of manganese on metal desulfurization that manganese is more electro-negative than iron. Hence for reaction

$$Mn_{(met)} + Fe^{2+}_{(sl)} = Mn^{2+}_{(sl)} + Fe_{(met)} \qquad \text{(VIII, 147)}$$

the equilibrium constant

$$K_{Mn} = \frac{a_{Fe} \cdot a_{Mn^{2+}}}{a_{Mn} \cdot a_{Fe^{2+}}} \geq \frac{N_{Fe} \cdot N_{Mn^{2+}} \cdot \gamma_{Mn^{2+}}}{N_{Mn} \cdot N_{Fe^{2+}} \cdot \gamma_{Fe^{2+}}} \qquad \text{(VIII, 148)}$$

should be appreciably greater than unity.

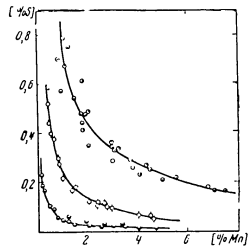

Fig. 189. Effect of manganese concentration and of temperature upon the contents of sulfur in cast-iron.
The upper plot is for 1600°C; the middle one - for 1400°C, and the lower one - for 1200°C.

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It is important to note herewith that the value of K_{Mn} is determined /see equation (VIII, 33)/ only be temperature and by the difference between the standard potentials of Fe and Mn, and not by the formulas of the presumed compounds. Indeed, for slags consisting almost exclusively of FeO and MnO, experiments /88/ yield the following empirical expression for the equilibrium constant

$$\lg \frac{(MnO)\,[Fe]}{(FeO)\,[Mn]} = \frac{6440}{T} - 2{,}95 \qquad \text{(VIII, 149)}$$

of the metal phase reaction with oxides

$$Mn_{(met)} + FeO_{(sl)} = MnO_{(sl)} + Fe_{(met)}. \qquad \text{(VIII, 150)}$$

Equation (VIII, 149) is quite similar to another one

$$\lg \frac{[MnS]\,[Fe]}{[FeS]\,[Mn]} = \frac{6000}{T} - 2{,}19\,, \qquad \text{(VIII, 151)}$$

derived /39/ for the reaction with sulfides

$$Mn_{(met)} + FeS_{(met)} = MnS_{(met)} + Fe_{(met)}. \qquad \text{(VIII, 152)}$$

The circumstance that reaction (VIII, 150) is heterogeneous, while interaction (VIII, 152) is homogeneous, is apparently of little importance. The fact of the matter is that the heats of FeS and MnS dissolution in slag should not, strictly speaking, affect the magnitude of the equilibrium constant. The temperature dependence of the latter is determined by the standard variation of free energy ($\Delta F^{\circ} = -RT\ln K$), which relates to the reactions occurring between the pure substances and not between their solutions.

The differences of the numerical coefficients in equations (VIII, 149) and (VIII, 151) are due mainly to the application of the ideal law of mass action. Actually, even for one and same reaction (VIII, 152) other authors /76/ produce a somewhat different expression for ΔF°, and consequently also for K

$$\Delta F^{\circ} = -25560 + 4{,}75\,T. \qquad \text{(VIII, 153)}$$

It is well known that the activities of basic oxides differ particularly sharply from the concentrations when appreciable quantities of SiO_2 are being introduced. For this reason the ideal law of mass action loses its validity, and equation (VIII, 149) for SiO_2 saturated slags has /89/ other coefficients

$$\lg \frac{(MnO)\,[Fe]}{(FeO)\,[Mn]} = \frac{7040}{T} - 3{,}172\,. \qquad \text{(VIII, 154)}$$

Thus manganese to a considerable degree expels iron ions both from sulfide and oxide melts. In view of this fact, the introduction of manganese into metal leads to a reduction in the concentration of Fe^{2+} ions (i.e., $N_{Fe^{2+}}$), which, according to equation (VIII, 141), explains the drop of sulfur contents in metal. On the other hand, with the fall of $N_{Fe^{2+}}$ the degree of metal's oxidation, i.e., /30/, diminishes too, and this, in turn /see equation (VIII, 142)/, also causes a drop of /88/.

Consequently, from the standpoint of the ionic theory the favorable effect of manganese consists in its displacement of iron ions from slag. This impedes the passage of sulfur from slag to metal and reduces the degree of latter's oxidation. Consequently it is incorrect to contrast the deoxidizing effect of manganese with its influence on the distribution of sulfur.

The opinion shared by a number of authors /38/, /39/, /67/, /90/, /91/, according to which — "the greater is the contents of manganese, the more effective is the deoxidation of metal and slag, and the more favorable are the conditions for the purification of metal from sulfur" /67/ — underscores only one aspect of the process. But it is, no doubt, correct and far more general than the application of the formula of solubility product, which is valid only for MnS saturated slags.

To elucidate the individual experimentally observed regularities, particularly those of expression (VIII, 144) which resembles the formula of solubility product, Yessin produced a derivation of relationship between the concentrations of sulfur (N_S) and manganese (N_{Mn}) in metal.

Let us consider the simplest case thereof when slag is composed only of FeS and MnS, with the metal containing but Fe, Mn, C, and S. With these limitations the following equations will be valid

$$N_{Fe} + N_{Mn} + N_C + N_S = 1, \qquad \text{(VIII, 155)}$$

$$N_{Fe^{2+}} + N_{Mn^{2+}} = 1\,, \qquad \text{(VIII, 156)}$$

$$N_{S^{2-}} = 1\,, \qquad \text{(VIII, 157)}$$

$$L_{FeS} = \frac{N_{Fe^{2+}} \cdot N_{S^{2-}} \cdot \gamma^{*}_{FeS}}{N_{Fe} \cdot N_S \cdot \gamma_S} = a\,\frac{N_{Fe^{2+}}}{N_{Fe}\,N_S}\,, \qquad \text{(VIII, 158)}$$

$$L_{MnS} = \frac{N_{Mn^{2+}} \cdot N_{S^{2-}} \cdot \gamma^{*}_{MnS}}{N_{Mn} \cdot N_S \cdot \gamma_S} = b\,\frac{N_{Mn^{2+}}}{N_{Mn}\,N_S}. \qquad \text{(VIII, 159)}$$

We determine $N_{Mn^{2+}}$ from expressions (VIII, 158) and (VIII, 159), and

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by replacing $N_{Fe^{2+}}$ and N_{Fe} in them from relationships (VIII, 155) and (VIII, 156) we find

$$N_{Mn^{2+}} = L'_{MnS} N_{Mn} N_S , \qquad \text{(VIII, 160)}$$

$$N_{Mn^{2+}} = 1 - L'_{FeS} N_S (1 - N_{Mn} - N_C - N_S). \qquad \text{(VIII, 161)}$$

Here

$$L'_{FeS} = \frac{L_{FeS}}{a} = \frac{L_{FeS}\gamma_S}{\gamma^s_{FeS}} , \qquad \text{(VIII, 162)}$$

$$L'_{MnS} = \frac{L_{MnS}}{b} = \frac{L_{MnS}\gamma_S}{\gamma^s_{MnS}} . \qquad \text{(VIII, 163)}$$

Since the contents of sulfur in metal is ordinarily small (less than 1%), it becomes possible to disregard N_S as the subtrahend in equation (VIII, 161). Excluding, further, the quantity $N_{Mn^{2+}}$ from formulas (VIII, 160) and (VIII, 161), we find

$$N_S = \frac{1}{L'_{FeS}(1 - N_C) + N_{Mn}(L'_{MnS} - L'_{FeS})} . \qquad \text{(VIII, 164)}$$

The obtained equation shows that only in the case when it is possible to neglect the addend in the denominator will the relationship between the contents of sulfur and manganese in metal be simple, reminding that of the formula pertaining to the solubility product

$$N_S \sim \frac{1}{N_{Mn}(L'_{MnS} - L'_{FeS})} . \qquad \text{(VIII, 165)}$$

In the general case the dependence is considerably more complicated. This apparently explains the reason for the existence of two types of empirical formulas

$$[\%\ S] = \frac{\alpha}{[\%\ Mn]} + \beta , \qquad \text{(VIII, 166)}$$

$$[\%\ S] = \frac{\alpha'}{[\%\ Mn]} . \qquad \text{(VIII, 167)}$$

Thus, for instance, Volovik /92/, in emphasizing the fact that manganese facilitates ex-furnace desulfurization of cast-irons, sets forth the following relationship. For open-hearth cast-irons which contain more than 1% Si and are covered by slag consisting of 37-39% SiO_2, the relationship between /%S/ and /%Mn/ conforms to equations

$$[\%\ S] = \frac{0{,}1025}{[\%\ Mn]} + 0{,}0165 , \qquad \text{(VIII, 168)}$$

$$[\%\ S] = \frac{0{,}0140}{[\%\ Mn]} + 0{,}0175 . \qquad \text{(VIII, 169)}$$

The first refers to metal at tap, the second - to metal delivered into the pouring machine.

Two analogous relationships

$$[\%\ S] = \frac{0{,}0339}{[\%\ Mn]} ; \quad [\%\ S] = \frac{0{,}0359}{[\%\ Mn]} , \qquad \text{(VIII, 170)}$$

valid for Bessemer cast-iron (> 1.3% Si) and slag with 37-39% SiO_2, unlike the above, do not contain a constant β.

Further, it is easy to obtain from equation (VIII, 164) an expression for the index of desulfurization

$$L'_S = \frac{(S)}{[\%\ S]} \cong \frac{1}{N_S} = L'_{FeS}(1 - N_C) + N_{Mn}(L'_{MnS} - L'_{FeS}). \qquad \text{(VIII, 171)}$$

It follows thereby that the value of L'_S must grow together with N_{Mn}.

As may be seen from fig. 190, the experiment /62/ confirms this to be so for diverse temperatures (from 1500 to 1900°C). Moreover, the equilibrium constant for reaction (VIII, 147), in the first approximation, is equal to the ratio L'_{MnS}/L'_{FeS}. Since $K_{Mn} > 1$ and drops with the rise of temperature, $L'_{MnS} > L'_{FeS}$, while the difference $(L'_{MnS} - L'_{FeS})$ diminishes also with T. It follows therefore that the slope of the straight-lines must increase with the lowering of temperature. The foregoing is in agreement with experimental data (see fig. 190).

Finally, the results of the investigations /42/ recorded in table 25 evidence that the product of /%Mn/ by /%S/ for steel is approximately double that for cast iron, and grows in both cases with temperature.

Table 25. Magnitude of the product /%Mn/ /%S/ for cast-iron and steel at different temperatures

Temperature, °C	/%Mn/ /%S/	
	cast-iron	steel
1425	0.59	—
1480	0.74	—
1540	0.93	2.0
1600	1.17	2.5
1650	1.48	3.2

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These facts can also be easily explained by means of equation (VIII, 164). Indeed, it follows from the latter that

$$N_{Mn} N_S = \frac{N_{Mn}}{\gamma_S \left[\frac{L_{FeS}}{\gamma^*_{FeS}} (1 - N_S) + N_{Mn} \left(\frac{L_{MnS}}{\gamma^*_{MnS}} - \frac{L_{FeS}}{\gamma^*_{FeS}} \right) \right]}. \qquad \text{(VIII, 172)}$$

It results therefrom that the smaller value of $N_{Mn} N_S$ in cast-iron is due to the presence in it of silicon and carbon which considerably increase the activity coefficient of sulfur.

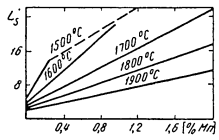

Fig. 190. Effect of the temperature and manganese contents in metal on the index of desulfurization L'_S.

Independent observations /83/ indicate that γ_S for cast-iron may (with one and same weight concentration of sulfur) be even as much as 5 times greater than in the case of steel. Furthermore, since L_{MnS} is greater than L_{FeS}, and drops faster with growing temperature, the use of equation (VIII, 172) helps to explain the experimentally observed increase of the value of $N_{Mn} N_S$ product with rising temperature.

Thus the ionic theory, departing from the fact that manganese is less noble than iron, is capable of explaining the regularities determined by experiment which are related to its influence on the completeness of cast-iron and steel desulfurization.

Let it be mentioned in conclusion that certain authors emphasize the accelerating effect produced by manganese upon the process of sulfur elimination from metal. Thus, for instance Karnaukhov /60/ believes that manganese, while exerting no direct influence on equilibrium, catalyses the reactions forming the intermediate compound MnS. Schematically the process is assumed to develop as follows

$$\begin{gathered} FeS_{(met.)} + Mn_{(met.)} = MnS_{(met.)} + Fe_{(met.)} \\ MnS_{(met.)} = MnS_{(sl.)} \\ MnS_{(sl.)} + CaO_{(sl.)} = MnO_{(sl.)} + CaS_{(sl.)} \\ MnO_{(sl.)} + C_{(met.)} = Mn_{(met.)} + CO_{(gas)} \\ \hline FeS_{(met.)} + CaO_{(sl.)} + C_{(met.)} = Fe_{(met.)} + CaS_{(sl.)} + CO_{(gas)}. \end{gathered} \qquad \text{(VIII, 173)}$$

A similar point of view was expressed by Zamoruev /93/, Panfilov /94/, Danilov /95/, and other authors /96/.

Danilov, in particular, in substantiating his considerations refers to fig. 191, from which it transpires that an increase of manganese concentration by 0.1% accelerates the rate of desulfurization, approximately, by 0.002% per hour.

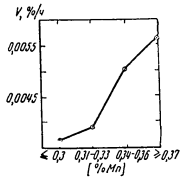

Fig. 191. Rate of sulfur removal versus manganese contents in metal.

At the present time there are no reasons whatsoever to deny either the catalytic power of manganese, or the latter's favorable influence upon the equilibrium distribution of sulfur between cast-iron and slag. From the ionic theory viewpoint the summary equation of Karnaukhov's reaction

$$S_{(met.)} + O^{2-}_{(sl.)} + C_{(met.)} = S^{2-}_{(sl.)} + CO_{(gas)} \qquad \text{(VIII, 174)}$$

emphasizes only the fact that carbon is a more powerful deoxidizer of metal than manganese. What it is then that constitutes the accelerative effect of the latter - remains still unknown.

EFFECT OF SILICA AND ALUMINA.

As mentioned previously, the addition of SiO_2 and Al_2O_3 as well as as other oxides forming poly-atomic anions leads to an increase of γ^2_{FeS}, i.e., to a drop of the desulfurization index. In addition to the material

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described before relative to the general influence of such oxides, let us revise certain data pertaining to the effects produced by them individually.

Thus, the effect of silica can be seen quite clearly from the diagram in fig. 192, which provides the lines of equal values of L_S' [82]. The diagram shows that the increase of SiO_2, if the relationship of CaO and FeO is given, causes a drop of L_S'. According to Karmazin [39], ferrous slags are affected by silica in a similar way.

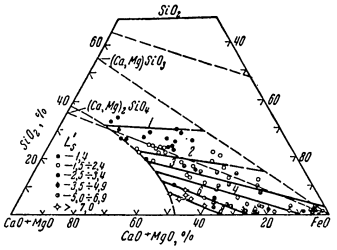

Fig. 192. Desulfurization index versus slag composition.

This fact, however, calls for additional explanation. The matter of the fact is that the activity of ferrous oxide in $FeO-SiO_2$ slags (in contrast to the more complex ones, such as, e.g., $FeO-CaO-SiO_2$) is about equal to its mole fraction [97], [98].

In this connection, it may seem to appear that γ_{FeO}, and consequently also γ_{FeS}, are equal to unity in this case, and that L_S' does not change upon SiO_2 addition. However, this is not so because for slags containing n_1 moles of FeO and n_2 moles of SiO_2 — i.e., consisting of n_1 Fe^{2+}, $(n_1 - 2n_2)$ O^{2-}, and n_2 SiO_2 — the mole fraction of FeO

$$N_{FeO} = \frac{n_1}{n_1 + n_3} = 1 - \frac{n_2}{n_1 + n_3} \qquad \text{(VIII, 175)}$$

is greater and it varies with growing SiO_2 less rapidly than the product of ionic fractions

$$N_{Fe^{2+}} \cdot N_{O^{2-}} = \frac{n_1 - 2n_2}{n_1 - n_2} = 1 - \frac{n_2}{n - n_2}. \qquad \text{(VIII, 176)}$$

It follows directly therefrom that γ^2_{FeS} equal to

$$\gamma^2_{FeS} \cong \gamma^2_{FeO} = \frac{a_{FeO}}{N_{Fe^{2+}} \cdot N_{O^{2-}}} \cong \frac{N_{FeO}}{N_{Fe^{2+}} \cdot N_{O^{2-}}}, \qquad \text{(VIII, 177)}$$

is greater than unity and increases alongside with the contents of silica. In other words, L_S' in this case must decrease with rising concentration of SiO_2.

Without dwelling any longer on similar data, we shall only remark that sometimes a positive influence of SiO_2 is also to be observed. However, this always takes place in the absence of equilibrium and is attributable to the decrease in slag viscosity resulting from the addition of SiO_2. In consequence thereof, the process develops more rapidly although the possible depth of desulfurization decreases.

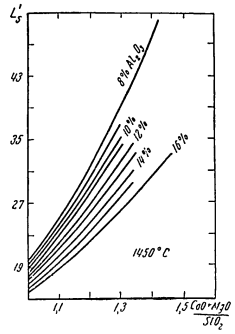

Fig. 193. Effect of basicity and silica contents in slag upon the index of desulfurization.

It is true that in certain cases the possibility is admitted for desulfurization to take place also under acid slags (40–50% SiO_2; 25–30% CaO; 18–20% Al_2O_3) in a reduction atmosphere at high temperatures. This is assumed to presuppose the development of reaction $FeS + SiO_2 + 2C = Fe + SiS + 2CO$. The temperature of the process may, it seems, be somewhat reduced by additions of small quantities of Na_2CO_3, CaF_2 or TiO_2.

The data produced by Voskoboynikov [99] may serve as a graphic illustration to the effect that silica also causes a drop of L_S'. As follows

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from fig. 193, the increase of Al_2O_3 concentration leads to a noticeable reduction of $L_S^!$ when the temperature is given and the $CaO:SiO_2$ ratio is fixed. For example, at 1450°C and with $CaO:SiO_2 = 1.2$, the desulfurization index for 8% Al_2O_3 slag is equal to 32.6, whereas at 16% Al_2O_3 it is lower, amounting only to 22.5.

Similar results were obtained [62] also for almost pure ferrous slags (with no more than 5% impurities, i.e., MgO and SiO_2), as well as for more complex varieties (FeO-MnO). It appeared that at 1600°C an addition of 30-40% Al_2O_3 reduces $L_S^!$ almost by 80%.

Finally, the fact that silica is present in slags in the form of polyatomic anions is also evidenced by the processing [55] of experimental data conducted in the assumption that silica is either inert, or that it forms aluminates $CaO \cdot Al_2O_3$ and $2CaO \cdot Al_2O_3$.

Fig. 194 reveals that the points resulting from calculations are contiguous to the so-called standard line, plotted for the simplest slags with the admission that Al_2O_3 is to be found in the form of $2\,CaO \cdot Al_2O_3$. This fact is by no means a proof of the existence of precisely such compounds in slag. It bears witness only to the effect that silica is not inert. By combining with oxygen, it produces some or other aluminate anion[1].

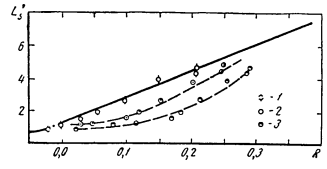

Fig. 194. Effect of Al_2O_3 on $L_S^!$

Solid line - standard. Points - experimental data calculated in the assumption that Al_2O_3 is present in the form of:
1 - $2CaO\,Al_2O_3$; 2 - $CaO\,Al_2O_3$; 3 - inert diluent.

1) However, according to Karmazin [109], Al_2O_3 under certain definite conditions passes into slag as a result of the treatment of metal by aluminum. The experiments conducted by Mikulinsky and Umova [101] evidenced a similar phenomenon. This indicates that there is a possibility that in definite cases not only anion complexes of aluminum, but also its cations, may be present in slag.

We shall now dwell on the influence of the replacement of Al_2O_3 for SiO_2. Experience shows that in the conditions of blast-furnace [71] such substitution contributes to a greater elimination of sulfur from cast-iron. Similar results were also produced by Mikhaylov and Utrobin [99], and later by Semik [70] in laboratory conditions. The latter conducted his tests in graphite crucibles for a period of 30 minutes using a small quantity of metal (thickness of the layer - 4 mm). These data are partially represented in table 26.

Semik attempted to relate this effect of Al_2O_3 only to the variation of the viscosity of slag which is hardly justifiable. As it may be seen from table 26 no explicit parallellism is to be observed between $L_S^!$ and η. Moreover, the sulfur contents in metal dropped sufficiently strongly (from 0.8 to 0.05%) during the test, and, as is revealed by the shape of the kinetic curve (fig.195), it evidenced hardly any tendency towards further appreciable variation.

Table 26. Effect of the replacement of SiO_2 by Al_2O_3 on the index of desulfurization at 1515°C.

Composition of slag %				$L_S^!$	η, poises
CaO	MgO	SiO_2	Al_2O_3		
50	—	35	15	47	2,9
50	—	40	10	31	3,4
35	15	35	15	16	3,2
35	15	40	10	15	2,7
40	15	36	9	32	1,8
40	15	31,5	13,5	94	2,0
30	25	36	9	42	1,7
30	25	31,5	13,5	45	7,2

The matter, apparently, is not in the kinetics of the process. The longer tests (75 min.) on cast-iron desulfurization carried out at 1500°C by Semkin seem to corroborate this conclusion. They also conspicuously displayed (table 27) a drop of sulfur percentage in metal upon replacement of SiO_2 by Al_2O_3.

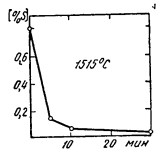

Fig. 195. Kinetics of cast-iron desulfurization.

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Most probably the favorable effect of the replacement of a part of silica by alumina is to be ascribed to the fact that one weight unit of Al_2O_3 immobilizes a lesser number of oxygen ions than SiO_2, for example,

$$SiO_2 + 2O^{2-} \rightarrow SiO_4^{4-},$$
$$Al_2O_3 + O^{2-} \rightarrow 2AlO_2^{-}.$$

Table 27. Effect of SiO_2 replacement by Al_2O_3 in slag on the contents of sulfur in cast-iron.

% Al_2O_3	Contents of sulfur in cast-iron, %, at			
	CaO + MgO = 45%		CaO + MgO = 50%	
	20% CaO	25% CaO	20% CaO	25% CaO
15	0,163	0,113	0,830	0,063
20	0,107	0,087	0,064	0,041
25	0,05*	0,058	0,057	0,033

EFFECT OF ALKALI-METAL OXIDES.

Various methods of ex-furnace desulfurization have been broadly practiced in cast-iron production for quite some time now.

Most frequently use is made of mixtures containing bases of alkali metal salts. Along with soda, suggestions were made for the use of sodium silicates [102], caustic soda individually and in combination with soda [86], a mixture of potassium, barium and strontium carbonates [85] calcium carbide[1] [103], sodium chloride together with calcium carbide, as well as the latter blended with metallic aluminum [39], and, finally, a mixture of slaked lime with table salt. A review of the patent and periodical literature covering this matter up to 1948 was made in an article by Volovik [92] (see also [83]).

According to Karnaukhov [69] the favorable influence of soda and similar additions is due to two[2] facts. On the one hand, the low melting point of the forming slags assures their small viscosity and a rapid change of composition at the reaction boundary. On the other hand, the application of the cited mixtures increases the desulfurization index L_S', i.e.,

1) Blown into molten metal with the aid of nitrogen.
2) Added here too should be the reduction of the interphase tension resulting from the introduction of Na_2O into slag [104]. The possibility is not excluded that this may facilitate the penetration of interphase boundary.

contributes to a deeper desulfurization of metal.

The latter fact can be explained from the viewpoint of the ionic theory, as before, by the microg-inhomogeneity of slag and the consequent decrease of the coefficient γ_{FeS} with increasing contents of basic oxides, in this case of Na_2O [69].

In full agreement with this, fig. 196 shows that the desulfurization effect, measured by the number of units in weight of extracted sulfur per unit of soda introduced into slag, turns out to be greater, the higher the initial concentration of S in metal and the greater is the $Na_2O:SiO_2$ ratio in slag.

The effect of K_2CO_3 is somewhat weaker (see fig. 196, dotted curve) than that of Na_2CO_3. However, this difference levels out considerably if the calculation is made not on the basis of 1 g, but on that of 1 mole of addition.

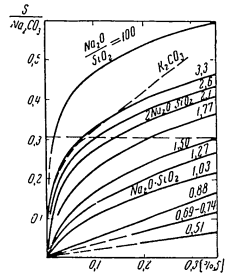

Fig. 196. Desulfurization of cast-iron by soda and sodium silicates.

The dotted horizontal line corresponds to the passage of the total quantity of sodium into Na_2S. The dotted curve - desulfurization by potassium.

The horizontal dotted line indicates the quantity of sulfur stoichiometrically corresponding to the soda introduced. The fact that a greater amount of sulfur actually passes into slag is an indication that the process cannot be reduced to the chemical reaction

$$Na_2O_{(sl)} + FeS_{(met)} = Na_2S_{(sl)} + FeO_{(met)},$$

but constitutes a distribution of sulfur between metal and slag.

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In consequence of silicon oxidation by air in cast-iron, the SiO_2 contents may increase in slag, which would cause a drop of L'_S. Therefore, the most advantageous results are ordinarily produced by desulfurization of low-silicon cast-irons.

In a number of cases a proportion of sulfur is oxidized by the oxygen of air

$$2S^{2-}_{(sl)} + 3O_{2\,(gas)} = 2O^{2-}_{(sl)} + 2SO_{2\,gas}$$

and is eliminated into the atmosphere in the form of SO_2. However, one should not overestimate the role of this reaction in the process of desulfurization, since the entire purifying operation in the ladle lasts only some 5 - 10 minutes.

Usually in the industrial conditions about 1% of Na_2CO_3 is taken with respect to the weight of cast-iron. This usually accounts for the extraction of 40 to 60% of the total sulfur contents in metal. Fig. 197 taken from the work by Volovkin [92] may serve as an illustration. The results which he obtained show that the addition of soda reduces the concentration of sulfur the more effectively, the greater its contents in metal.

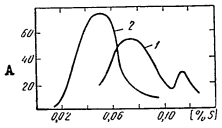

Fig. 197. Sulfur contents in cast-iron 1) before and 2) after its treatment by soda.

A - Number of experiments.

In his opinion, in order to obtain metal of specified composition, it is necessary to proportion the addition of soda as indicated in table 28.

Table 28. Consumption of soda and relative desulfurization at different initial contents of sulfur in cast-iron.

Initial sulfur contents, %	Relative consumption of Na_2CO_3 in relation to the weight of cast-iron, %	Relative desulfurization, %
0,05—0,07	0,57	30,5
0,07—0,09	0,67	41,0
0,09—0,11	0,74	52,9
0,11—0,13	1,01	58,8
0,13—0,15	1,09	61,3
0,15—0,17	1,18	67,2

According to Volovik a substantial reduction of soda consumption may be achieved by its partial replacement by manganocalcite $CaMn(CO_3)_2$. Their mixture composed of equal amounts by weight acts even more effectively (by 20-30%) than pure soda.

INFLUENCE OF TEMPERATURE

The published data dealing with the effect of the temperature on the index of desulfurization are quite contradictory. Some authors believe that L'_S diminishes, others - that it increases, with growing temperature. The latter point of view is held, for instance, by Voskoboynikov [99] and Joseph with his co-workers [65], [71]. Karmazin [38], [39] and a number of other investigators [62], [55] share the first opinion, i.e., that L'_S decreases with rising temperature.

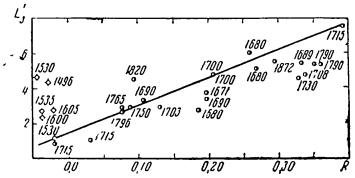

Fig. 198. Desulfurization index L'_S versus basicity R at different temperatures.

Furthermore among the second group of investigators there also exist divergences. Some believe [62] that the desulfurization index drops considerably with increasing temperature in cases of ferrous slags (see fig. 190) and propose the following equation for its calculation

$$\lg L'_S = \frac{2390}{T} - 0{,}714. \qquad \text{(VIII, 178)}$$

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Others, upon analysis of data covering slags of a very motley composition, come to the conclusion [55] that L_S' grows very slowly when temperature is falling. Fig. 198 serves as an illustration for this case and refers to experimental heats run at temperatures ranging from 1496 to 1820°C. The data for all temperatures are grouped comparatively closely along a single "standard" line.

The opinion that L_S' diminishes somewhat with growing temperature appears to be more correct, although this also calls for additional proofs. As to the opposite data, they apparently pertain to non-equilibrium states. As a matter of fact, the rate of the establishment of an equilibrium sulfur distribution is relatively low and grows with temperature.

Consequently, in those conditions (particularly in production), where equilibrium is not achieved, the ratio (S):[S] may grow with temperature in view of the acceleration of the process rate. Such apparently was the situation during the investigations of Voskoboynikov, Samarin, and Teodorovich, and a number of other authors.

In conclusion, let us remark that certain authors [55] on the basis of the fact that L_S' drops with rising temperature while the equilibrium constant of reaction (VIII, 100) which proceeds with heat absorption, on the contrary, increases, come to the erroneous conclusion that reaction (VIII, 100) does not determine the equilibrium distribution of sulfur.

Meanwhile, if equilibrium is established, then the equations are equally valid for L_S and L_O as well as for K_S. The fact that K_S, equal to

$$K_S = \frac{a_O \cdot a_{S^{2-}}}{a_S \cdot a_{O^{2-}}} = \frac{L_S}{L_O}, \qquad \text{(VIII, 179)}$$

increases with temperature, while L_S, on the contrary, diminishes, actually indicates only that L_O drops with the growth of T more rapidly than L_S. No conclusion regarding the process determining the system's equilibrium could be drawn therefrom.

As a result of an analysis [105] of the experimental data produced by a number of investigators, a formula was proposed for the temperature dependence of the equilibrium constant

$$\lg \frac{1}{K_S} = \lg \frac{N_S \cdot N_{O^{2-}}}{N_O \cdot N_{S^{2-}}} = \frac{6500}{T} - 2{,}625. \qquad \text{(VIII, 180)}$$

Here N_S and N_O = atomic fractions of sulfur and oxygen in metal;

$N_{S^{2-}}$ and $N_{O^{2-}}$ = ionic fractions calculated in the regular way (not on the basis of the theory of perfect ionic solutions)

From equation (VIII, 180) it follows that K_S grows with temperature, whereas the desulfurization reaction is accompanied by heat absorption (30 Kcal/g-atom).

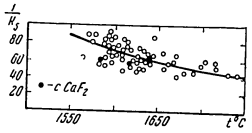

Fig. 199. Effect of temperature on the magnitude of $1/K_S$.

Fig. 199 represents the relationship (VIII, 180) and the individual experimental points.

ON THE KINETICS OF DESULFURIZATION

In spite of the great practical significance of the desulfurization process, the available published material on its kinetics is very limited. Below we shall consider the investigations pertaining to the rates of the processes of sulfur removal by air oxygen and by slag.

Oxidation by Oxygen.

In the work by Samarin and Schwartzmann [106] an attempt was made to study the kinetics of the burn-out of sulfur and other elements under direct action of air oxygen on liquid metal while by-passing slag as an intermediate phase.

They believe that they succeeded in keeping the metal surface continuously exposed by freezing slag around an iron rod.

The independence of the process of sulfur and carbon combustion was established. It turned out that in Fe-C-S alloys the rate of sulfur oxidation, when all other conditions are equal, is the same as for Fe-S alloys. Processing of the experimental data showed that the logarithm of sulfur concentration diminishes linearly with time (fig. 200).

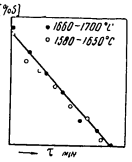

Fig. 200. Kinetics of the burn-out of sulfur from its alloy with iron under the influence of air.

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Hence it follows that the rate v of the process is directly proportional to sulfur concentration c

$$v = -\frac{dc}{dt} = kc . \qquad \text{(VIII, 181)}$$

It was also established that the rate constant k does not change practically with temperature ($0.27 \cdot 10^{-2}$ min.$^{-1}$ over the interval 1560-1700°C). In this connection a conclusion was made to the effect that the element's diffusion inside the metal constitutes the limiting stage of the oxidation process.

Then

$$k = \frac{D}{\delta} \cdot \frac{S}{m} = k' \frac{S}{m} . \qquad \text{(VIII, 182)}$$

where D = diffusion coefficient;
S = interface area;
m = mass of metal;
δ = thickness of the unstirred metal layer.

Making use of this relationship, the authors calculated the diffusion coefficient of the enumerated elements on the basis of their studies of the oxidation rates of S, C, Mn, Si, and the published data on the kinetics of nitrogen absorption. Assuming that the value of δ is the same in all cases, i.e., considering

$$\frac{D_1}{D_2} = \frac{k_1'}{k_2'} ,$$

they obtained $D_{Mn} = 9.6$; $D_{Si} = 7.39$; $D_N = 3.26$; $D_C = 2.83$; and $D_S = 1.66$ cm^2 per 24 hours.

The produced diffusion coefficient series give rise to doubts. It is known, for instance, that in Gamma-iron both the absolute value of coefficients D_i, and the order of their arrangement are different [107], namely: $D_{C,925°C} = 935$; $D_{N,800°C} = 104$, and $D_{Si,960°C} = 65$ cm^2/24 hours. Besides, according to the measurements of Stark, Chelishchev and Kazachkov [108], D_{Si} in liquid iron is approximately, 1.7 times greater than D_{Mn}.

It is, further, unclear how the independence of k from temperature could be reconciled with the diffusion character of the process and the work in the induction furnace. The fact of the matter is that the regulation of temperature is achieved here only by variation of the current strength I. The intensity of the mixing of metal, on the other hand, is proportional to I^2. If the process has a diffusion character, then the rise of temperature should affect δ and k conspicuously.

Finally, there is no adequate certainty that the oxygen of air had actually affected only the exposed metal. One cannot totally bar the chance that a portion of sulfur was oxidized from slag. The possibility of such a process was discussed by Kryanin, who believes that during the smelting of steel in convertors with side blowers the oxygen of air oxidizes sulfur dissolved in slag.

Desulfurization by Slag (Qualitative Pattern).

A number of investigators have noted that the establishment of equilibrium sulfur distribution between metal and slag proceeds very slowly. Thus, for instance, Semik [70] finds that sulfur equilibrium in graphite crucibles cannot be attained during a period of 30 minutes even with small quantities of metal (10-15 g) and slag. In view of this the ratio (S):[%S] must depend considerably on the viscosity of slag[1].

Voskoboynikov [99] records data (table 29) on the smelting of 100 g of cast-iron, which contained 1.5% S, and 60 g of slag (41% SiO_2, 12% Al_2O_3, 47% CaO) at a temperature of 1450°C. As it may be seen from the tabulated figures, equilibrium was only established after two hours.

Table 29. Variation of sulfur contents in cast-iron and slag with time.

Time, min.	[%S]	(%S)	(%S):[%S]
5	0.44	1.51	3.4
15	0.36	1.86	5.2
30	0.20	2.07	10.3
90	0.09	2.30	25.6
180	0.086	2.35	27.3

According to Lindeman [111] the time needed for the establishment of equilibrium in acid slags is even greater. Finally, Samarin, Schwartzmann, and Temkin [18] note that the small value of L_S^1 (0.02 instead of 0.08), determined earlier [67], points to the low speed with which equilibrium is being attained in industrial aggregates.

A question arises in connection with the foregoing as to what constitutes the factors determining the kinetics of metal desulfurization by slag. No doubt, diffusion conditions must prevail in a number of cases, since the change of slag viscosity affects the rates of the process. However, there are reasons to believe that the transfer of sulfur from metal to slag also proceeds sufficiently slowly.

1) Consequently, the measures designed to assure a reduction of slag viscosity always produce a positive effect on desulfurization. In particular, the introduction of small quantities of Al_2O_3 into slag [41], [66], [109], [110], which reduce appreciably its viscosity, constitutes one of the most popular methods of desulfurization speed-up.

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This can be gathered particularly from laboratory tests [11] in which the rate of cast-iron desulfurization, depending on the temperature and slag composition, was studied. These experiments showed that the rate of the process, related to the unit of specific interface area, does not depend on mixing (tests with rotating and stationary crucibles). Apparently the change of composition in the reaction area produced by gaseous CO, liberated as a result of the reaction, proceeds intensively enough.

It is quite probable that in this case the kinetics of desulfurization are not determined by the rate of diffusion or convection. The considerable magnitude of the apparent activation energy of sulfur transfer from metal to slag (79 Kcal) determined by the authors, also speaks in favor of this fact. Finally, the dependence of the activation energy on the composition of slag indicates that the chemical reaction occurring within the metal also does not limit the development of the process. All this contributes to the assumption [22] that the kinetics of desulfurization in these tests (provided they can be considered sufficiently accurate) were apparently determined by the event proper of penetration of the metal-slag interface.

The authors [11] proceed from the molecular theory of slags, according to which the desulfurization process of cast-irons is constituted [62], [82] by the transfer stage of the particles of ferrous sulfide from one phase into another

$$FeS_{(met)} \rightarrow FeS_{(sl)}, \qquad \text{(VIII, 183)}$$

of the homogeneous reaction in slag

$$FeS_{(sl)} + CaO_{(sl)} \rightarrow FeO_{(sl)} + CaS_{(sl)}, \qquad \text{(VIII, 184)}$$

and the stage of carbon burn-out

$$FeO_{(sl)} + C_{(met)} = CO_{(gas)} + Fe_{(met)}. \qquad \text{(VIII, 185)}$$

Moreover, they, like a number of other authors [42], believe that stage (VIII, 183) constitutes the slowest process. However, this assumption provides no explanation of certain regularities established by them. In particular, this pertains to the non-reclinear drop of the rate with the growth of sulfur concentration in slag and to the effect of the latter's composition upon the rate constant of the forward reaction.

The authors used cast-iron with a considerable contents of carbon (3.88-5.12% C), while the temperature was sufficiently high (1525-1580°C). The passage of bivalent iron ions into slag, as well as the presence in it of trivalent iron, would have seemed to be improbable in such highly reductive conditions. In other words, the penetration of sulfur ions from metal into slag

$$S_{(met)} + 2\Theta \rightarrow S^{2-}_{(sl)} \qquad \text{(VIII, 186)}$$

should have been accompanied by the process

$$O^{2-}_{(sl)} - 2\Theta \rightarrow O_{(met)}, \qquad \text{(VIII, 187)}$$

instead of transitions

$$Fe^{2+}_{(sl)} + 2\Theta \rightarrow Fe_{(met)}, \qquad \text{(VIII, 188)}$$

$$2FeO^{-}_{2(sl)} + 2\Theta \rightarrow 2Fe^{2+}_{(sl)} + 4O^{2-}_{(sl)}. \qquad \text{(VIII, 189)}$$

Moreover, the oxygen penetrating into metal would have reacted with the carbon dissolved in same and evolved in the form of CO

$$C_{(met)} + O_{(met)} = CO_{(gas)}. \qquad \text{(VIII, 190)}$$

In spite of all this, an attempt has been made in a more recent work [13] to prove experimentally that a transfer of FeS molecules from metal to slag takes place at least at the beginning of the process. The authors revealed the existence of iron in slag by chemical analysis, and endeavored to prove by a series of special tests that it is present not in the form of minor beads (ejected by evolving gas) but in the form of molecules of a chemical compound. If one assumes the latter to be FeS, then reaction (VIII, 184) is limiting. If, on the contrary, one should consider this to be FeO molecules, then the combustion of carbon would constitute the rate determining event.

The passage of iron ions, and particularly of FeS molecules, into slag seems to be highly questionable. However, even in assuming this to be true, one should rather accept another explanation [120] according to which the process develops as per reaction (VIII, 40)

$$S_{(met)} + O^{2-}_{(sl)} \rightarrow S^{2-}_{(sl)} + O_{(met)},$$

whereby, due to the slowness of reaction (VIII, 190), the oxidation by oxygen primarily of iron takes place up to a definite moment according to reaction (VIII, 39')

$$O_{(met)} + Fe_{(met)} = Fe^{2+}_{(sl)} + O^{2-}_{(sl)}.$$

In any case, transitions (VIII, 39') and (VIII, 190) proceed parallelly. Consequently, even considering the slowness of one of them, for

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example (VIII, 190), it is still possible to assume that reaction (VIII, 40) is the one which determines the rate of the entire process of sulfur transition from metal to slag /22/.

Comparison of Equations with Experimental Data.

To demonstrate the advantages of the ionic theory, let us compare the corollaries ensuing from equations (VIII, 61) and (VIII, 62) with those which result from the molecular hypothesis. In the latter case, the two following alternatives are possible.

The first, as already mentioned, infers that the intensity of desulfurization is determined by the rates of FeS molecule transition from metal to slag. Then, owing to the small concentrations of FeS in both phases, the process rate will comprise

$$v = k_1 [FeS] - k_2 (FeS). \qquad \text{(VIII, 191)}$$

In the second alternative desulfurization is limited by chemical reaction between the molecules of CaO and FeS in slag. Since the stages of FeS transition into slag and FeO into metal are considered here to be rapidly developing (acting to achieve equilibrium), the rate determining reaction may be recorded as heterogeneous

$$CaO_{(sl)} + FeS_{(met)} = CaS_{(sl)} + FeO_{(met)}. \qquad \text{(VIII, 192)}$$

This point of view constitutes the closest molecular analogue of the ionic theory, since the reduction in reaction (VIII, 192) of Ca^{2+} cations and $Fe_{(met.)}$ atoms leads directly to process (VIII, 40).

Considering the fact that of all four reacting substances (CaO, FeO, CaS, and FeS) in the experiments involved only the CaO concentration was comparatively large, it seems to be worth while to discuss the isotherm of adsorption with fractional exponent ($0 \leq z \leq 1$) only with respect to CaO. Hence

$$v = k_1' [FeS] (CaO)^z - k_2' [FeO] (CaS). \qquad \text{(VIII, 193)}$$

From now on we shall consider the concentrations of sulfur and oxygen in metal to be constant for any given temperature. As regards sulfur, this condition was achieved experimentally by a corresponding selection of metal and slag volumes. The contents of oxygen, according to equation

$$[O][C] = kp_{CO} \qquad \text{(VIII, 194)}$$

was determined by the concentration of carbon and by partial pressures of CO. The former, as shown by chemical analyses, remained constant throughout the entire test. The latter, i.e., p_{CO}, in the furnace provided with a graphite crucible, could also be considered as undergoing negligible changes.

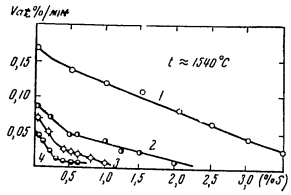

Fig. 201. Rate of sulfur transition from cast-iron into slag depending on the contents of sulfur in slag and the basicity of same.

Curve	1	2	3	4
Al_2O_3, %.....	15	15	15	15
CaO, %.....	45	40	35	30
SiO_2, %.....	40	45	50	55

For a comparison of equations (VIII, 62), (VIII, 191), and (VIII, 193), the data produced by tests /112/, after conversion of the concentration of sulfur in slag from weight into atomic percentage, were plotted in a graph with coordinates (S^{2-}) and time t. The rate was graphically determined for a number of points according to the smooth curves produced.

The calculated transition rates v are functions of the concentration x of sulfur in slag. Graphically they are represented by curves drooping towards the X-axis with their bulges facing same. Exemplifying the foregoing is fig. 201 which displays a family of such curves. Each of them differs from the other, mainly, by the ratio of CaO to SiO_2.

As may be seen from the diagram, the drop of v is slowed down with the growth of x, which fact is in full agreement with equation (VIII, 62). This, on the other hand, does not follow from the equations for both alternatives of the molecular theory. Indeed, if /FeO/ = const, then they both produce a linear relationship between v and x.

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The authors [112] endeavored to explain the retardation of the v drop by the variation of the activity coefficient of sulfur. However, this explanation seems hardly probable for solutions so strongly diluted and for slags with constant basicity. Whatever may be the case, the ionic theory equations do not call for a resort to sulfur activity coefficients — which up to this moment remain still practically unstudied — for the explanation of the relationship of v against x.

Moreover, if one assumes that [FeO] is not constant but proportional to (CaS) — since it is on the parallelism of the sulfur contents in iron and slag that these and other authors in a more recent work [113] insist — then it transpires from the second alternative of the molecular hypothesis that

$$\frac{\partial v}{\partial x} = -2k'_2 x < 0; \quad \frac{\partial^2 v}{\partial x^2} = -2k'_2 < 0, \qquad \text{(VIII, 195)}$$

i.e., that the drop of the process rate with growing sulfur concentration in slag should, on the contrary, be accelerated with the increase of x.

Only by postulating high capillary activity either of FeS, or of CaS, i.e., the requirement for the exponent z to be fractional, it becomes possible to bring both molecular versions into accord with facts.

Actually, in this case

$$\frac{\partial v}{\partial x} = \frac{k_3 z}{(\mathrm{FeS})^{1-z}} < 0; \quad \frac{\partial^2 v}{\partial x^2} = \frac{k_3 z(1-z)}{(\mathrm{FeS})^{2-z}} \quad 0 \qquad \text{(VIII, 196)}$$

or

$$\frac{\partial v}{\partial x} = \frac{k'_3 z\,[\mathrm{FeO}]}{(\mathrm{CaS})^{1-z}} \quad 0; \quad \frac{\partial^2 v}{\partial x^2} = \frac{k'_3 z(1-z)\,[\mathrm{FeO}]}{(\mathrm{CaS})^{2-z}} \quad 0. \qquad \text{(VIII, 197)}$$

However, such concordance calls again for special conjectures, whereas the ionic theory requires none.

We shall now pass over to the next characteristic. Fig. 201 shows that the initial speed corresponding to the condition x = 0 increases not only with the contents of sulfur in metal but also with the basicity of slag. Equation (VIII, 62) is in harmony with this fact. Yet, the cited regularity cannot be obtained from equation (VIII, 191) while it follows from expression (VIII, 193). In this respect the second alternative of the molecular theory produces formally the same result as the ionic.

However, it again fails to explain the facts when dealing with the third singularity pertaining to the tangent of the v(x) curve at point x = 0.

From fig. 201 it follows that the fall of the curve v(x) at the initial point is the steeper, the lower the basicity of slag. This fact transpires readily from expression (VIII, 62), but it does not absolutely follow from the equations of either of the two molecular theory versions.

Finally, the fourth peculiarity consists in that the apparent activation energy of the forward reaction, as disclosed by fig. 202 plotted against the data of the tests [112], drops from 114,500 to 58,400 cal when the contents of CaO in slag increases from 35 to 50%. The recorded fact is in perfect agreement with equation (VIII, 62), but it can hardly be interpreted on the basis of the first version of the molecular hypothesis, while the second alternative, apparently, does not contradict it.

The aforesaid shows therefore that from the positions of the ionic theory it appears to be fairly easy to explain the experimentally established singularities of the kinetics of cast-iron desulfurization. The molecular concepts, on the contrary, are unable to provide the answers in a number of instances even when special assumptions are made.

It goes without saying, that the above is true subject to sufficient reliability of the pertinent experimental data. Further experimentation in this domain is very much needed.

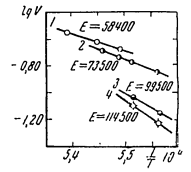

Fig. 202. Initial rate of cast-iron dephosphorization versus temperature for slags of different composition

Curve	1	2	3	4
CaO, %	50	45	40	35
SiO_2, %	35	40	45	50
Al_2O_3, %	15	15	15	15

3. DEPHOSPHORIZATION REACTION.

For the majority of the steel brands phosphorus is a harmful impurity reducing the mechanical properties of metal. In view of this, great attention is given in the manufacture of steel to the process of dephosphorization.

As is well known, the removal of phosphorus from metal is usually

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made with the aid of slag. Laboratory investigations into this interaction, conducted with the application of the radioactive isotope P^{32}, show [115], [116] that an equilibrium distribution of phosphorus can be achieved in a relatively short period of time (according to one set of data in 1-5 min., according to other sources in 10 - 15 min.). The same is indicated by certain technological observations [117].

Consequently, investigations into the equilibrium of the reaction under consideration assume a particularly great significance for the purpose of defining the best conditions for desulfurization. The material available in literature on the effects of temperature and slag composition upon the equilibrium distribution of phosphorus is discussed below from the viewpoint of the ionic theory.

This is prefaced with a survey of the forms in which phosphorus is to be found in both liquid phases.

MODES OF PHOSPHORUS EXISTENCE IN LIQUID METAL AND SLAG.

At the present moment there are four known chemical compounds of phosphorus with iron-Fe_3P, Fe_2P, FeP, and FeP_2 - whose standard heats of formation comprise 35,200, 34,500, 25,000, and 34,000 cal/mol. respectively [12]. Metallurgically the first two compounds present an essential interest. A certain amount of information concerning their stability is provided by the fusibility diagram of the Fe - P system (fig. 203) plotted originally by Konstantinov [118] and somewhat elaborated for precision subsequently by other investigators [119].

As may be seen from fig. 203, phosphide Fe_3P melts incongruently and disintegrates at a temperature exceeding 1166°C. Moreover, its separation from the melt during cooling occurs only upon inoculation with Fe_3P seeds. In the absence of these, a different compound separates from the liquid phase, namely Fe_2P, and the crystallization proceeds in conformity with the diagram of the labile range (see dotted lines in fig. 203).

These facts point to a different coordination of atoms in the lattice of Fe_3P and in liquid phase. They emphasize the fact of a substantial redistribution of particles during the melting of Fe_3P phosphide. On the other hand, a conspicuous maximum at the liquidus line and the ready separation of Fe_2P crystals speak of the structural similarity of the melt and the lattice[1]).

In spite of these facts, suggesting that the most probable mode of phosphorus existence in liquid iron is constituted by the Fe_2P groups,

1) It should be noted that in a series of similar systems, Co-P in particular, the Me_3P compound is absent, whereas a fairly sharp maximum at the liquidus line corresponds usually to Me_2P compounds.

a number of authors share a different opinion. Thus, for example, Schenk [61], in order to reconcile the experimental data on metal and slag equilibrium with the law of mass action, inferred that phosphorus is present in liquid metal in the form of $(Fe_3P)_2$ polymers.

Others [42], on the contrary, believe that the presence in iron of elementary phosphorus is "unquestionable". In view of this, in their physico-chemical analysis of the process, they proceed from "the theory of the elementary state of phosphorus".

The assumption concerning the $(Fe_3P)_2$ polymers and the "free" atoms of phosphorus contradicts the constitution diagram and disagree with the heats of phosphide formation. Even if it were possible to speak here of dissociation, then it would be only of the removal of an iron atom from Fe_3P, since it is only this process that is accompanied by a minor thermal effect [11]

$$3Fe + P = Fe_3P; \qquad \Delta H = -35\,200 \text{ cal/mol}$$
$$2Fe + P = Fe_2P; \qquad \Delta H = -34\,500 \text{ cal/mol}$$
$$\overline{Fe_3P + Fe = Fe_3P}; \qquad \Delta H = -700 \text{ cal/mol}$$

As stated previously, investigation of high-temperature galvanic cells, in which liquid alloys of iron with phosphorus and carbon served as electrodes, confirmed the existence in molten metal of a stable Fe_2P compound. There is only one explicit inflection on the e.m.f. vs %P in alloy curve located near the point corresponding to 22% P and, consequently, to Fe_2P (see fig. 165).

Within the Fe_2P groups homeo-polar bonds are probably predominant [11]. The considerable thermal effect and the absence of electrolytic effect during the passage of direct current through the alloy [13] speak in favor of this fact.

Apart from this, experiments revealed that phosphorus reduces the surface and interphase tensions of iron. In the presence of the very stable bonds between P and Fe, this is possible only in the case that quasi-molecules of Fe_2P, and not atoms of phosphorus, are being expelled onto the interface.

All the facts disclosed above permit one to believe that phosphorus is to be found in liquid cast-iron and steel in the form of Fe_2P, and not in that of Fe_3P as was sometimes assumed in the past [82].

As to molten slag, phosphorus here is apparently present in the form of PO_4^{3-} if the basicity is sufficiently high. Indeed, x-ray diffraction studies, for instance, of calcium-phosphate glasses [121] show that the principal structural unit in them, as in the case of silicates, is the PO_4 tetrahedron.

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Consequently, when there is an excess of O^{2-} ions in slag it is hardly possible to expect the formation of anions with a higher number of oxygen atoms per atom of phosphorus than in PO_4^{3-}.

EQUILIBRIUM OF THE SIMPLEST FERROUS SLAGS.

Unlike sulphur, phosphorus is transferred into slag by means of combining its atoms with those of oxygen

$$Fe_2P_{(met)} + 4\,O^{2-}_{(sl)} = 2\,Fe_{(met)} + PO^{3-}_{4\,(sl)}. \qquad \text{(VIII, 198)}$$

The compensating process which liquidates the continuous accumulation of electrons in metal is thereby constituted of the transition of iron ions

$$2{,}5\,Fe^{2+} + 5\,\Theta = 2{,}5\,Fe. \qquad \text{(VIII, 199)}$$

Thus, to realize a total reaction

$$Fe_2P_{(met)} + 4\,O^{2-}_{(sl)} + 2{,}5\,Fe^{2+} = 4{,}5\,Fe_{(met)} + PO^{3-}_{4\,(sl)} \qquad \text{(VIII, 200)}$$

it is necessary for the slag to contain O^{2-} and Fe^{2+} ions, i.e., ferrous oxide.

Indeed, the latter, even in a pure state, is capable, as evidenced by tests, of extracting a certain amount of phosphorus from metal.

Considering the complexity of the process, it seems practical to dwell first of all on the survey of the simplest ferrous slags, i.e., on the system

$$Fe - P/FeO - P_2O_5.$$

The equilibrium constant for reaction (VIII, 200) may then be recorded as

$$K = \frac{a^{4,5}_{Fe} \cdot a_{PO_4^{3-}}}{a_{Fe_2P} \cdot a^4_{O^{2-}} \cdot a^{2,5}_{Fe^{2+}}}. \qquad \text{(VIII, 201)}$$

At small phosphorus concentrations in metal the activity of iron is close to unity, while the activity coefficient of phosphorus is small, though practically constant, since the Fe_2P phosphide is stable enough [117].

Considering the aforesaid and after introduction of the ionic fraction

for slags, we find from equation (VIII, 201) the distribution index to be

$$L' = \frac{(P_2O_5)}{[P]} \simeq \frac{N_{PO_4^{3-}}}{N_P} = K_1 \cdot N^4_{O^{2-}} \cdot N^{2,5}_{Fe^{2+}} \cdot \frac{\gamma^4_{O^{2-}} \cdot \gamma^{2,5}_{Fe^{2+}}}{\gamma_{PO_4^{3-}}}. \qquad \text{(VIII, 202)}$$

The expression thus obtained shows that the relationship between the phosphorus concentrations in metal and slag is sufficiently complex even in the reviewed simplest case where $N_{Fe^{2+}} = 1$. It cannot be linear, because $N_{O^{2-}}$ drops with growing $N_{PO_4^{3-}}$ and the values of all activity coefficients change. Neither can it be reduced to a quadratic relationship if for no other reason because the product of $\gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}}$ varies exponentially with the contents of PO_4^{3-} as was mentioned earlier (see page 507).

In this connection the old argument as to whether the relationship between (P_2O_5) and [P] should be represented by a parabola [122] or by a straight-line [123], [124], [61] is immaterial. According to Kamensky's and Abrosimov's well grounded observation [117], the spread of the points in these graphs is so large that it is impossible to make any reliable conclusions on their basis. Fig. 204 containing the data of a number of authors [76] may serve as an illustration thereof.

The equilibrium of reaction (VIII, 200) for ferrous slags was recently studied by Schwartzmann and Gruzin [116] with the aid of radioactive isotope P^{32} over a temperature interval ranging from 1500 to 1780°C. Since the concentration of PO_4^{3-} in slag was small, $N_{O^{2-}} \cong 1$, while all $\gamma_i \cong$ const.

In other words, the equilibrium constant was numerically equal to the distribution index

$$L' = K = \frac{N_{PO_4^{3-}}}{N_P} = \frac{I_{(sl)}}{I_{(met)}} \qquad \text{(VIII, 203)}$$

and differed little from the ratio of specific radioactivities (I) of both phases at the moment of equilibrium.

Fig. 205 shows that the data produced may be, with sufficient approximation, described by equation

$$\lg K = \frac{9000}{T} - 5{,}30. \qquad \text{(VIII, 204)}$$

To put it another way, reaction (VIII, 200) is exothermic developing with a release of 21 Kcal per gram-atom of P. The value of K ordinarily is

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smaller than unity and the equilibrium is shifted to the left. A purely ferrous slag, therefore, cannot assure any appreciable depth of metal desulfurization.

Schwartzmann and Gruzin [116] calculated further the value of the coefficient

$$K' = \frac{N_{PO_4^{3-}}}{N_P \cdot N_{O^{2-}}^4 \cdot N_{Fe^{2+}}^{2,5}} \qquad \text{(VIII, 205)}$$

from the experimental data produced by other investigators for the temperature interval 1500-1550°C.

The results of these computations, recorded in fig. 206, point to a very regular increase of K' with $N_{PO_4^{3-}}$. In this manner, on the basis of the theory of perfect ionic solutions, they succeeded in reconciling the experimental material of various authors, which until then was considered contradictory.

Since the value of K' approaches that of K when $N_{PO_4^{3-}} \longrightarrow 0$, the rise of K' with growing $N_{PO_4^{3-}}$ is due solely to the increase of the activity coefficients. More precisely, the quantity γ which is equal to

$$\gamma = \frac{K'}{K} = \frac{\gamma_{O^{2-}}^4 \cdot \gamma_{Fe^{2+}}^{2,5}}{\gamma_{PO_4^{3-}}} = \frac{\gamma_{O^{2-}}^{1,5} \cdot \gamma_{FeO}^5}{\gamma_{PO_4^{3-}}}. \qquad \text{(VIII, 206)}$$

grows alongside with the concentration of PO_4^{3-} ions in slag.

It was noted earlier that the coefficient γ_{FeO} augments considerably with increasing concentration of polyatomic anions (SiO_4^{4-}, AlO_2^-, PO_4^{3-}, etc.) in slag. It seems, that this fact also causes a considerable growth of γ, the magnitude of which includes the fifth power of γ_{FeO}.

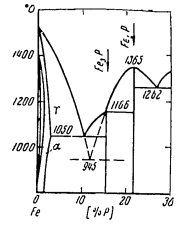

Fig. 203. Fusibility diagram of the iron-phosphorus system.

Dotted lines - metastable state of system.

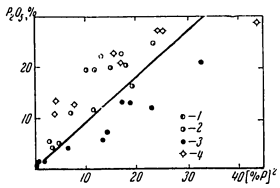

Fig. 204. Phosphorus concentration in metal versus phosphorus contents in slag according to the data:

1 - re. [122]; 2 - re. [61]; 3 - Fe. [123]; 4 - re. [124].

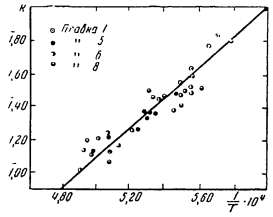

Fig. 205. Equilibrium constant K versus temperature according to equation (VIII, 204).

Points - experimental data.

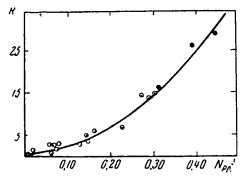

Fig. 206. Coefficient K' in formula (VIII, 205) versus $N_{PO_4^{3-}}$ according to the data of various authors.

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EFFECT OF CALCIUM OXIDE.

The purely ferrous slags do not assure the required degree of phosphorus elimination. This is due to the great energy of interaction of the Fe^{2+} and O^{2-} ions, which strongly diminishes their activity. This fact, in turn, provokes a shifting of equilibrium (VIII, 200) to the right.

The forces drawing the O^{2-} ions to Fe^{2+} are so great that the PO_4^{3-} becomes fairly unstable in the vicinity of an iron cation. Actually, the thermal effect of iron phosphate formation is considerably less than those of manganese, calcium, and particularly barium, phosphates [105].

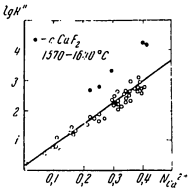

Fig. 207. Relationship between the ionic fraction of Ca^{2} and the constant K" in equation (VIII, 209).

In order to attain the desired degree of dephosphorization of metal, it is necessary to introduce into slag other cations which do not interact so powerfully with O^{2-} anions. Of the cations Mg^{2+}, Ca^{2+}, Fe^{2+}, and Mn^{2+} which are usually present in it, the weakest from this point of view is Ca^{2+} (the greatest radius).

To what extent its additions are effective can be gathered from the following results. It was previously stated that the increase of basicity, of CaO contents in particular, diminishes strongly the coefficient γ_{FeO}. To evaluate this fact we shall make use of the empirical relationship recorded earlier (see page 339).

$$\gamma^2_{FeO} = \gamma_{Fe^{2+}} \gamma_{O^{2-}} = \frac{1}{N^{2.5}_{O^{2-}}}. \qquad \text{(VIII, 207)}$$

and introduce it into the expression for the equilibrium constant

$$K'' = \frac{N_{PO_4^{3-}}}{N_p \cdot N^{2.5}_{Fe^{2+}} \cdot N^{0.25}_{O^{2-}}} = K \frac{\gamma^{1.5}_{O^{2-}}}{\gamma_{PO_4^{3-}}}. \qquad \text{(VIII, 208)}$$

The magnitude of K" does not depend on the activity coefficient of iron ions and, at a given temperature, it is entirely determined by the ratio of the similar coefficients for oxygen and phosphate anions. As it may be seen from fig. 207, plotted against experimental date, its logarithm grows in direct proportion to the ionic fraction of Ca^{2+} [105] according to equation

$$\lg K'' = \lg K + \lg \frac{\gamma^{1.5}_{O^{2-}}}{\gamma_{PO_4^{3-}}} = 7 N_{Ca^{2+}} + \frac{14\,600}{T} - 7.44. \qquad \text{(VIII, 209)}$$

Thereupon[1], considering relationship (VIII, 204) we have

$$\lg \gamma' = \lg \frac{\gamma^{1.5}_{O^{2-}}}{\gamma_{PO_4^{3-}}} = 7 N_{Ca^{2+}} + \frac{5660}{T} \quad 2{,}14 \qquad \text{(VIII, 210)}$$

Thus, the activity coefficients of PO_4^{3-} ions and the quantity K" prove to be very sensitive to the contents of calcium ions in slag. A rise in $N_{Ca^{2+}}$ increases sharply the value of K" and, consequently, displaces the equilibrium considerably to the right.

From this standpoint, even better results could be expected in consequence of BaO introduction into slag [105]. The difference in thermal effects of $Ba_3(PO_4)_2$ and $Mg_3(PO_4)_2$ formation attains 57 Kcal. per gram-ion, whereas for $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ this represents only 24.6 Kcal.

In other words, the stability of the PO_4^{3-} anion increases considerably upon the replacement of Ca^{2+} by Ba^{2+}. If the introduction of Ca^{2+} increases sharply the shift of the equilibrium for reaction (VIII, 200) in the desired direction, then even a greater effect should be achieved through addition of BaO. Regrettably, no experiments have been carried out in this direction so far.

JOINT EFFECT OF CALCIUM AND FERROUS OXIDES.

In evaluating the role of FeO and CaO in the removal of phosphorus from metal, it should always be borne in mind that reaction (VIII, 200) becomes impossible in the absence of iron cations (i.e., FeO). No matter how useful the Ca^{2+} ion might be, it still is capable only of shifting the equilibrium (VIII, 200) in the desired direction. This, though, is totally

1) Expression (VIII, 210) is not quite accurate, because the ionic fractions in formula (VIII, 209) were calculated by routine method, whereas in equation (VIII, 204) this was made on the basis of the theory of perfect ionic solutions.

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unfeasible in the absence of Fe^{2+}, or some other cations, capable of passing into metal. This can be gathered, for instance, from equation (VIII, 202), from which it follows that L' vanishes when no iron cations are present in slag.

On the other hand, in the absence of calcium cations the activity of O^{2-} anions is small, which fact does not permit one to attain the necessary degree of dephosphorization. It is obvious that there exists some optimum relationship between the concentrations of CaO and FeO which corresponds to the maximum removal of phosphorus from metal.

Actually, tests confirm this to be so as is illustrated [19] by fig. 208. Here, for each given ratio of CaO to SiO_2, the curve — plotted according to coordinates L' and CaO/FeO (weight percentage) — reveals a maximum distribution index corresponding to the least contents of phophorus in metal.

In order to supply a qualitative explenation for the regularities observed during dephosphorization, we shall substitute the quantity γ_{FeO}^{2} in equation (VIII, 202) by means of equation (VIII, 207). Then

$$L' = \frac{(P_2O_5)}{[P]} = K_1 N_{O^{2-}}^{0,25} N_{Fe^{2+}}^{2,5} \cdot \gamma'. \qquad \text{(VIII, 211)}$$

Let us now revert to the experimental data available in literature. Thus, for instance, laboatory tests [12] show that an increase of calcium oxide in CaO – FeO – P_2O_3 slags initially augments the distribution index and then lowers it. Fig. 209 provides a number of such isotherms with L' maxima, which indicate that the optimum contents of calcium oxide amounts to around 60 mol. %.

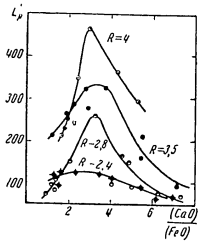

Fig. 208. Relationship between the dephosphorization index L'_P and the ratio of the weight percentages of CaO and FeO in slag at different basicities of same (R = CaO:SiO_2).

In the recorded case the growth of CaO concentration, on the one hand, causes a drop of the ionic fraction of iron $N_{Fe^{2+}}$, while on the other hand, it is responsible for the increase of $N_{O^{2-}}$, and particularly γ^{1}, as follows from equation (VIII, 210). Such mutually opposed effect of the cofactors in expression (VIII, 211) leads to the appearance of the maximum value of L'.

The existence of an optimum concentration of CaO is confirmed by a number of other investigators [12], [12] also for more complex slags. As a matter of fact, analysis of the results of 250 heats leads to the conclusion [12] that the most advantageous basicity value is

$$\frac{CaO}{SiO_2 + P_2O_5} = 2,5 - 2,8.$$

Thus, the growth of CaO within certain limits leads to the increase of L', in spite of the diminishing percentage of FeO. Such unilateral influence of calcium oxide was noted in many works, particularly in those by Gorin [12], and by Umrikhin and Kokarev [12]. It may be seen from table 30, for example, that in the process of slag formation during the period of metal melting a regular growth of the distribution index is to be registered together with the increase of the $CaO:SiO_2$ ratio, although the FeO concentration is simultaneously dropping in slag [12]. Analogous results are recorded in the works by Kamensky and Abrosimov [11], Samarin [7], Schenk [6], and other authors.

Table 30. Variation of L' with Slag Composition

Heat	Sample	Metal composition, %			Characteristic of slag		
		P	C	Mn	CaO/SiO_2	FeO %	L'
I	1	0,041	2,72	0,10	0,87	16,8	73
	2	0,032	2,42	0,10	1,03	15,8	108
	3	0,021	1,29	0,13	1,05	7,8	108
	4	0,011	1,01	0,18	2,62	12,6	132
II	1	0,055	0,92	0,12	0,75	40,06	14
	2	0,031	0,81	0,10	1,30	12,25	43
	3	0,023	0,74	0,08	1,55	11,80	50

Passing over now to the opposite case, when the contents of ferrous oxide increases in slag while the concentration of CaO diminishes, let us note that the value of L' must also have a maximum here. Indeed, although the factors $N_{O^{2-}}$ and $N_{Fe^{2+}}$ increase in equation (VIII, 211) the value of γ' still falls together with $N_{Ca^{2+}}$.

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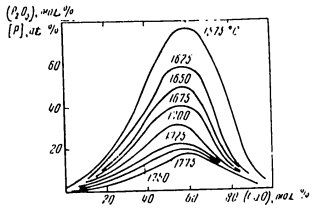

Fig. 209. Effect of the concentration of calcium oxide in slag upon the index of phosphorus distribution at different temperatures.

Fig. 210 constitutes an experimental confirmation thereof. It shows that the growth of FeO contents facilitates the removal of phosphorus only to a definite limit, which to a certain extent depends on the relationship of CaO to SiO_2. As a first approximation this optimum corresponds to 15% FeO. Thus, to assure successful elimination of phosphorus from metal, it is important for the slag to contain a very definite proportion of FeO and CaO.

So far only such cases were considered where the optimum value of that or the other factor was manifestly displayed. However, the experimental conditions and the method of data expression may be selected in such a manner that the distribution index might appear as a monotonic function without extremes.

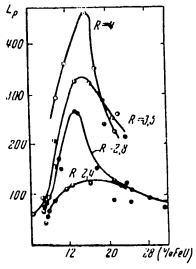

Fig. 210. Index of phosphorus distribution versus ferrous oxide contents in slag and basicity R.

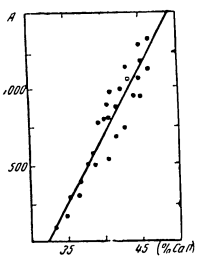

Fig. 211. Effect of calcium oxide concentration in slag on the quantity

$$A = \frac{1}{|P|} \cdot \frac{(P_2O_5)}{(P_2O_5) + (FeO)}$$

Thus, for instance, if L' is divided by $N_{Fe^{2+}}^{2.5}$, then according to equation (VIII, 211), the relationship produced

$$\frac{L'}{N_{Fe^{2+}}^{2.5}} = K_1 N_{O^{2-}}^{0.25} \cdot \gamma' \qquad \text{(VIII, 212)}$$

must continue to increase with growing CaO concentration. In a measure this fact is reflected in fig. 211, where plotted along the Y-axis is the quantity

$$\frac{1}{|P|} \cdot \frac{(P_2O_5)}{(P_2O_5) + (FeO)}.$$

It increases almost linearly with growing calcium oxide contents [130].

The monotonic variation of the distribution index follows also from fig. 212, in which, within the triangle of compositions, there are represented [131] the lines of equal values for the quantity

$$L'' = \frac{(4\,CaO \cdot P_2O_5)}{|P|^3}.$$

By fixing various constant FeO contents, i.e., by tracing straight-lines parallel to the side representing $CaO-SiO_2$, we find that in this case the experimentally determined coefficient L'' increases continuously together with the contents of the bases. In other words, the growth of the latter's concentrations facilitates the removal of phosphorus. The aforesaid is in accord with equation (VIII, 211), following which the distribution index increases with CaO contents when the ionic fraction $N_{Fe^{2+}}$ is fixed. Indeed, the growth of CaO contents leads to an increase of $N_{O^{2-}}$ and γ'.

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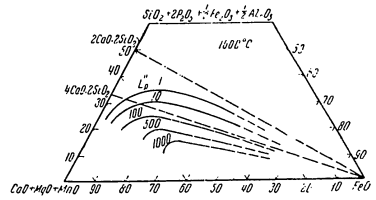

Fig. 212. Dependence of the index of phosphorus distribution

$$L''_P = \frac{(4CaO \cdot P_2O_5)}{[F]^2}$$ upon the composition of slag (mol.%).

By analogy thereto, the value of L" augments systematically with FeO contents if the percentage of the basic oxides, CaO in particular, is constant. In other words, in these conditions the growth of FeO contents only improves the indexes of the dephosphorization process.

This apparently is due to the fact that the increase of the ionic fractions $N_{O^{2-}}$ and $N_{Fe^{2+}}$ outweighs here the possible reduction of γ' caused by the strengthening of the anion's bond with slag (replacement of Ca^{2+} by Fe^{2+}).

The recognized fact of a continuous improvement of metal dephosphorization with increasing %FeO, when the CaO contents is fixed, was repeatedly confirmed under not only laboratory but also industrial conditions. In particular, a clear-cut parallelism between the degree of dephosphorization and the concentration of FeO was observed by Umrikhin [132], whose data are reported in table 31.

Table 31. Relationships between the contents of phosphorus in metal and the composition of slag.

Contents in slag (%) of			[% P]
FeO	Al_2O_3	CaO + MgO	
7,99	6,50	42,95	0,056
9,23	6,73	39,93	0,042
9,68	5,16	39,12	0,040
10,39	1,82	41,98	0,041
11,97	5,94	44,10	0,032
13,05	6,00	41,06	0,032
14,26	8,30	38,00	0,026
18,98	6,10	44,15	0,027

As it may be seen from the table, increasing FeO contents assures a more complete elimination of phosphorus when the total of CaO + MgO is constant. Similar data may also be found in the monographs by Karnaukhov [60], Trubin and Oyks [42], Schenk [61], in the studies of other authors [117], [128], and so on.

However, the same fig. 212 also shows that the monotonic variation of the distribution index is not possible in all conditions. Indeed, when the contents of SiO_2, P_2O_5, Al_2O_3 and similar oxides are fixed, the straight line drawn parallelly to the CaO–FeO side twice intersects the line of equal values of L".

To put it differently, in these circumstances the increase of CaO or FeO concentration (more precisely – the replacement of Ca^{2+} ions by those of Fe^{2+} and vice versa) contributes only to a certain extent to phosphorus removal from metal. The distribution index attains a maximum value at a certain optimum FeO:CaO ratio.

The foregoing is also in perfect agreement with equation (VIII, 21). Actually in the case of question $N_{O^{2-}}$ = const. The factor $N_{Fe^{2+}}$ grows with increasing FeO contents. But since % CaO drops at the same time, the ionic fraction $N_{Ca^{2+}}$ diminishes too. This fact causes a decline of the second multiplier, namely γ'. As a result of mutually opposed changes of $N_{Fe^{2+}}$ and γ', the quantity L' passes through a maximum.

In conclusion let us remark again, that the roles of Ca^{2+} and Fe^{2+} in the process of dephosphorization are not equivalent. This transpires clearly from the comparison of equations (VIII, 210) and (VIII, 211) which leads to the expression

$$L' = \frac{(P_2O_5)}{[P]} = K_2 N_{O^{2-}}^{0,25} \cdot N_{Fe^{2+}}^{2,5} \cdot 10^{7 N_{Ca^{2+}}}. \qquad \text{(VIII, 213)}$$

The latter shows that the influence of the concentration of Ca^{2+} ions is many times greater than that of Fe^{2+} ions. Yet, in the absence of the first, i.e., when $N_{Ca^{2+}} = 0$, the removal of sulfur from metal is still possible to a certain extent because, the terminal value of L' is

$$L' = K_2 N_{O^{2-}}^{0,25} \cdot N_{Fe^{2+}}^{2,5}. \qquad \text{(VIII, 214)}$$

On the other hand, if there are no iron ions in slag, then the process is altogether impossible and the distribution coefficient is equal to zero at any given basicity.

The greater effect of calcium oxide than that of ferrous oxide on desulfurization can also be seen [19] from the empirical equation

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$$\lg \frac{(P_2O_5)}{[P]^2} = 13{,}6 \lg (CaO) + 5 \lg (FeO) - 25{,}97. \qquad \text{(VIII, 215)}$$

However, it is not valid [19], [105] when the values of (CaO) are small and does not, therefore, reflect the possibility of a partial elimination of phosphorus in the absence of calcium oxide in slag.

EFFECT OF MANGANOUS AND MAGNESIUM OXIDES.

The radius of the Mn^{2+} ion (0.91 Å) is conspicuously larger than that of Fe^{2+} (0.83 Å), in consequence of which the energy of interaction of the O^{2-} anion with the former is smaller than with the latter.

Hence, upon partial replacement of FeO by MnO the activity of the oxygen ions should increase, with equilibrium (VIII, 200) shifting in the direction of more complete desulfurization of metal. In this respect the effect of MnO is analogous to the influence of CaO, since in both cases the value of γ' augments, though in varying degrees.

However, the concentration of iron ions, i.e., $N_{Fe^{2+}}$, drops at the same time, in view of which fact the distribution coefficient L' will grow upon the addition of MnO, as per equation (VIII, 211), only to a certain limit. In other words, here, as in the case of calcium oxide, one should expect to find an optimum relationship of MnO to FeO for which the maximum L' value is to be registered.

The favorable effect of MnO admixtures will also prevail when, without changing $N_{Fe^{2+}}$, they increase the basicity of slag, i.e., the concentration of O^{2-} anions.

The foregoing explains the observations repeatedly described in the literature, according to which the increase of manganous oxide concentration in slag leads to a decline of phosphorus contents in metal. Some authors [61] erroneously have believed that this effect is due to the growth of free calcium oxide caused by its expulsion from silicates by manganous oxide. The useful effect of MnO additions on dephosphorization was confirmed also by other investigators [131], who found its influence to be equivalent to that of calcium oxide at MnO contents up to 12%.

It should, nevertheless, be noted that the radius of the ion of Mn^{2+} is smaller than that of Ca^{2+} ion (1.06 Å). For this reason the replacement of MnO for CaO should lower the activity of O^{2-} anions and affect unfavorably the process of dephosphorization.

Similar facts are also to be found in the literature, as illustrated in fig. 213, which reveals [19] that with (%FeO) > 12 the distribution coefficient L' drops with the growth of MnO contents. An increase of the latter was accompanied by a reduction of CaO percentage.

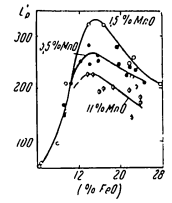

Fig. 213. Effect of the concentrations of ferrous and manganous oxides on the distribution index of phosphorus $L'_P = \frac{(P_2O_5)}{[P]^2}$.

Passing over to the influence of MgO, let us note that, although the Mg^{2+} ion radius (0.78 Å) is smaller than that of the Fe^{2+} cation, the latter is still somewhat stronger than the former owing to considerable polarizability. It is precisely this that accounts for the fact that the energy of the FeO crystal lattice (900 Kcal/mole) is greater than that for MgO (940 Kcal/mole) while the elasticity of dissociation of $FeCo_3$ is higher than in the case of $MgCO_3$ (see part I, page 272).

For this reason the introduction of Mg^{2+} ions, like that of Ca^{2+} and Mn^{2+} cations, may cause the activity of oxygen anions to increase, though very negligibly. In the meantime, the coefficient γ' remains constant or grows slightly. The replacement of CaO or MnO by MgO should harmfully affect the process of dephosphorization, since it is apt to cause a decrease of γ'. The substitution of MgO for FeO, on the other hand, though contributing slightly to the growth of γ', nevertheless leads to an essential drop of $N_{Fe^{2+}}$ which results in a decrease of L'.

The beneficial influence of manganous oxide should consequently manifest itself most conspicuously in the case when its introduction is made at the cost of a reduction of acid and amphoteric oxides. Yet, since $N_{O^{2-}}$ enters into equation (VIII, 211) with the exponent of only 0.25, then, in this case too, one should expect but a minor positive effect as a result of MgO addition.

Experimental data pertaining to the study of the effect of manganous oxide upon the distribution of phosphorus are regrettably scarce. Thus, according to Karnaukhov [60], manganous oxide in conformity with the aforesaid should not affect appreciably the equilibrium of the dephosphorization reaction. However in highly basic slags additions of MgO may lower the rate of the process owing to increasing viscosity. Approximately the

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same is the evaluation of the role of manganous oxide in the judgment of Schenk [61], who considers it as an indifferent diluent which does not practically affect the equilibrium of the system.

A different point of view is held by other authors [131] who believe that, when manganous oxide contents reaches up to 20%, its effect differs little from the influence produced by CaO. However, it is hardly possible to agree with this.

EFFECT OF ALUMINA AND SILICA.

In basic slags alumina and silica play the role of acid oxides. Combining with oxygen ions into complex anions they reduce the magnitude of $N_{O^{2-}}$ diminishing thereby the value of the distribution coefficient. The unfavorable influence on the process of dephosphorization becomes particularly strong, when along with the contents of O^{2-} anions a drop is to be registered also of the concentration of the cations of calcium - see equation (VIII, 213).

Thus, for instance, at a given $CaO:SiO_2$ ratio and FeO contents in slag, the addition of Al_2O_3 leads to a lowering of the concentrations of O^{2-} and Ca^{2+} ions.

As may be seen from fig. 214, this causes [19] the index of dephosphorization to drop considerably (1.7 times). According to the same data [19] additions of Al_2O_3 in less basic slags ($CaO:SiO_2 = 3.5$, instead of 4) produce a somewhat weaker influence causing L' to drop only 1.4 times. Similar results are also reported in other studies [131], [61].

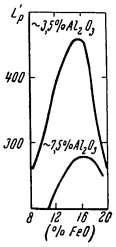

Fig. 214. Effect of aluminum and ferrous oxides on the index of phosphorus distribution L_P in basic slags ($CaO:SiO_2 = 4$).

It must be mentioned, however, that in a number of cases investigations into industrial heats have disclosed a favorable effect of alumina on the removal of phosphorus from metal. This fact was referred to, for

instance, by Einstein and Nesterov [133], Umrikhin [134], [132] and other investigators. However, the matter under discussion here does not concern equilibrium conditions but the kinetics of the process. Silica accelerates the formation and the fluidity of slag.

As regards silica, its harmful effect on the index of phosphorus distribution is similar to that of alumina and was discussed earlier. It remains to be added only that the restitution of phosphorus observed in industrial conditions is often caused not merely by the decline in FeO concentration, but also by the reduction of the CaO contents in consequence of the growth of % SiO_2. This happens in particular during deoxidation of metal, and consequently also of slag, by ferrosilicon.

EFFECT OF CALCIUM FLUORIDE.

The introduction of calcium fluoride produces a very favorable effect on the process of dephosphorization. It is known that it accelerates the formation of slag and causes it to become more fluid.

Consequently it is often recommended to serve as a component of various synthetic mixtures used for ex-furnace phosphorus elimination from metal [42].

Regrettably, its influence on equilibrium distribution of phosphorus has been highly insufficiently studied. In discussing the experimental data, certain authors [131] came to the conclusion that calcium fluoride constitutes but a diluent of slag and does not practically affect phosphorus distribution. Others [105], on the contrary, having recalculated the data of the above authors, find that CaF_2 additions cause, approximately a tenfold increase of the constant K", determinable by equation (VIII, 208).

In fig. 207, where log K" is plotted as a function of the concentration of Ca^{2+} ions, several points are recorded for slags containing CaF_2. As may be seen from this diagram the cited points are located considerably above the straight-line which characterizes the dependence of log K" upon the concentration of Ca^{2+} ions.

However, the above authors [105] interpret erroneously the fact they themselves have established of the strong influence of CaF_2 additions on the constant K". They assume incorrectly that the utilization of equation (VIII, 207) for the deduction of expression (VIII, 208) eliminates all activity coefficients, with the exception of one - $\gamma_{PO_4^{3-}}$. In other words, they maintain that the magnitude of K" depends entirely on the coefficient $\gamma_{PO_4^{3-}}$ included in the denominator of relationship (VIII, 208).

To explain the growth of K", they are compelled to assume the formation of complexes of F^- and PO_4^{3-}. Their appearance reduces the activity of PO_4^{3-} anions, i.e., lowering the value of $\gamma_{PO_4^{3-}}$, and this, in turn, involves the growth of K".

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However, the favorable influence of calcium fluoride may, it seems, be explained without resort to questionable postulates concerning the existence of complex anions consisting of F^- and PO_4^{3-} ions.

The fact of the matter is that CaF_2 contains a uni-negative anion. Hence, the replacement of a proportion of CaO by CaF_2, i.e., O^{2-} by $2F^-$, implies a lowering of the ionic fraction of Ca^{2+}, which these authors have calculated in the normal way by relating the number of Ca^{2+} cations to the total number of ions (and not to the sum only of all cations).

In order to assure that the ionic fraction of Ca^{2+} should remain the same it is still necessary to add a certain quantity of CaF_2 into slag. But then the ratio of the contents of Fe^{2+} and Ca^{2+} should change in favor of the latter. In other words, the bonds of the oxygen anions with the melt would diminish and their activity coefficient $\gamma_{O^{2-}}$ would increase involving the growth of the coefficient K" [see equations (VIII, 208) and (VIII, 210)].

EFFECT OF MANGANESE.

In the discussion of the desulfurization process, it was emphasized that, from the standpoint of the ionic theory, the most essential moment in the interpretation of the role of manganese is the fact that it expels the iron ions from slag. A strong decline of their concentration causes, according to equation (VIII, 211), a drop of the distribution coefficient L', or a growth of phosphorus contents [P], if all other conditions are equal.

Thus, the presence of manganese in metal may impede the removal of phosphorus therefrom. This is confirmed by tests. Thus, a relatively long time ago Karnaukhov [60] took notice of the fact that manganese in certain conditions reduces phosphorus from slag. These observations were later experimentally confirmed by other investigators [117], [135].

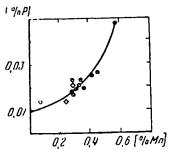

Fig. 215. Phosphorus contents in metal versus manganese concentration in same. Circles - data according to Kamensky and Abrosimov [117]. Points - according to [135].

Fig. 215 shows the regular growth of phosphorus concentration in metal containing increasing manganese contents. Kamensky and Abrosimov [117] arrived at the same conclusions after having processed the data of 111 test runs in 100-ton capacity open-hearth furnaces. Moreover, some heats were run with additions of spiegeleisen and manganese ore, others without them.

It should be mentioned, however, that Mn^{2+} cations appear in slag as a result of the expulsion of Fe^{2+} ions by manganese. The former interact more weakly with the anions of oxygen which causes a certain rise of the coefficient γ'. Consequently, the negative effect of manganese additions will persist so long as there remains a relatively small proportion of FeO and a comparatively large amount of MnO in slag. But it is precisely such a situation that arises in metal in the presence of large quantities of manganese because of its greater electro-negativity than that of iron.

On the other hand, when manganese is practically absent, then a partial replacement of FeO by MnO may be achieved in the conditions of relative predominance of iron ions. In this case the values of L' will be located on the other side of the curve maximum, where the growth of coefficient γ' outweighs the drop of $N_{Fe^{2+}}$ concentration. Then MnO additions to slag will reduce the contents of phosphorus in metal.

Kamensky and Abrosimov [117], in analyzing the experimental data [135], noted a number of cases when the contents of phosphorus continued to grow in metal in spite of the increase of slag basicity. They ascribe this fact to the lowering of the activity of phosphorus in metal due to the formation of manganese phosphide. By way of additional argument, they indicate that the ratio of phosphorus and manganese concentration increments corresponds approximately to the formula of Mn_5P_2 phosphide.

If the stability of the latter exceeds that of iron phosphide (and this seems to be so, though there is no direct confirmation to this effect), then the above conclusions should be considered justified. Introduction of manganese into metal will cause γ_P to drop, and will consequently, if all other conditions are equal, contribute to the growth of phosphorus contents.

COMPUTATION FORMULAS REFLECTING THE EFFECTS OF TEMPERATURE AND COMPOSITION.

The overwhelming majority of investigators in deriving computation formulas for the equilibrium constant of dephosphorization reaction proceed from the molecular theory of structure of liquid slags and from the applicability of the mass action law. Moreover, it was suggested that there takes place thereby in slag mostly the formation of weakly dissociated calcium tetraphosphate and only in individual cases that of triphosphate.

In addition to this, various meagerly substantiated assumptions have frequently been made to justify the derivation of formulas for equilibrium constants. The result of all this was that the produced relationships became purely empirical.

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Either analytic concentrations or free oxide contents were substituted for activities in the equilibrium constant expressions for dephosphorization reactions recorded in one form or another.

The method of computation of the contents of free oxides depends on the selection of the forms for the compounds contained in slag and also on the evaluation of the magnitudes of their dissociation constants.

To exemplify this type of relationship we shall cite the formula of Schenk and Riess [61]

$$\lg K = \lg \frac{[\Sigma P]\,(FeO)^5\,(CaO)^4}{(\Sigma P_2O_5)} + 0{,}06\,(\Sigma P_2O_5) = -\frac{51\,800}{T} + 35{,}05\,, \qquad \text{(VIII, 216)}$$

where $[\Sigma P]$ and (ΣP_2O_5) = total contents of phosphorus in metal and of its oxide in slag;

(FeO) and (CaO) = concentrations of free oxides not combined into silicates and phosphate;

$0.06\,(\Sigma P_2O_5)$ = addend introduced purely empirically and compensating, according to the authors, for the inaccuracies of computation and the undervaluation of the non-ideal nature of the melt.

A critical analysis of this material, made by Kamensky and Abrosimov [117], led them to the conclusion that expression (VIII, 216) is less satisfactory than the more simple equation

$$\lg K = \lg \frac{[P]^2\,(FeO)^5\,(CaO)^4}{(\Sigma P_2O_5)} = -\frac{51\,875}{T} + 33{,}16\,. \qquad \text{(VIII, 217)}$$

In both cases the calculation method of concentrations of free and combined oxides was the same, only the experimental data being different.

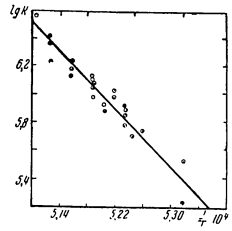

Fig. 216. Temperature dependence of K according to equation (VIII, 217)
Points - experimental data.

Fig. 216 displays a straight-line corresponding to equation (VIII, 27), and the points obtained from the elaboration of the results of 50 test heats in 100-ton capacity furnaces. The relatively narrow temperature interval investigated — from 1604 to 1674°C — should be noted.

The authors quite reasonably underline the fact that their formula "does not represent the magnitude of the true equilibrium constant; this is rather a singular coefficient which resembles the equilibrium constant only by form. Consequently, the use of the resulting expression for precise thermodynamic calculations would be wrong, to say the least" [117].

Other authors [131] produce a different evaluation variant of their laboratory tests from the positions of the molecular theory of slags. Unlike Schenk, they (again without sufficient substantiation) assume the existence in basic slags of the following compounds: $4CaO \cdot 2SiO_2$; $2CaO \cdot 2SiO_2$; $4CaO \cdot P_2O_5$; $CaO \cdot Fe_2O_3$; $CaO \cdot Al_2O_3$; $4CaO \cdot P_2O_5 \cdot CaF_2$ and of the free oxides CaO and FeO.

The formula produced by them has the aspect of

$$\lg K = \lg \frac{(4\,CaO \cdot P_2O_5)}{[P]^2\,[O]^5\,(CaO)^4} = \frac{77\,667}{T} - 28{,}73\,. \qquad \text{(VIII, 218)}$$

Here [P] and [O] are given in weight percentage, while (CaO) and $(4CaO \cdot P_2O_5)$ - are in mole fractions.

To what extent this expression encompasses the experimental data can

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be seen from fig. 217.

However, a re-calculation of these experimental data effected by Kozheurov [136], reveals that the computation method used by the authors [131] fails to assure a sufficient constancy of the quantity K. For different heats the value of $K^{1/5}_{1600^\circ C}$ varies from 19.8 to 120.3 with divergences most frequently attaining twice the value or less (from 66.7 to 120.3).

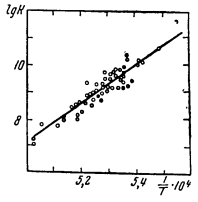

Fig. 217. Effect of temperature on the magnitude of K as per equation (VIII, 218).

Points represent the data pertaining to slags containing CaF_2.

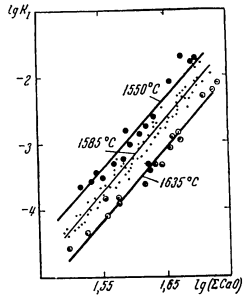

Fig. 218. Dependence of constant K_1 according to equation (VIII, 219) upon the total (analytic) contents of calcium oxide in slag and temperature.

Certain investigators [19], without applying the method of free and combined oxides, find that calcium oxide should enter into the equilibrium "constant" equation in a very high degree of concentration. They record their measurements, for example, by the following expression

$$\lg K_1 = \lg \frac{(P_2O_5)}{[P]^2 (FeO)} = 11{,}8 \lg (CaO) - C_1. \qquad \text{(VIII, 219)}$$

All concentrations in it correspond to analytic concentrations, while the value of C_1 grows with temperature from 21.13 at 1550° to 21.91 at 1635°C. The linear relationship established by these authors between log K_1 and log (CaO) is plotted in fig. 218 for various temperatures.

Furthermore they state that the data produced by previous investigators [131] also satisfy their empirical equation (VIII, 219).

From the point of view of the ionic theory the equilibrium of the dephosphorization reaction was investigated recently by Herasymenko [105]. He introduced ordinary ionic fractions (not according to the theory of perfect ionic solutions) into the equilibrium constant expression, while determining the dependence of the corresponding activity coefficients on composition by a purely empirical method. The expression which he produced constitutes

$$\lg K'' = \lg \frac{N_{PO_4^{3-}}}{N_P \; N^{2.5}_{Fe^{2+}} \; N^{0.25}_{O^{2-}}} = 7 N_{Ca^{2+}} + \frac{14\,060}{T} - 7{,}44. \qquad \text{(VIII, 220)}$$

In his opinion, equation (VIII, 220) agrees satisfactorily with the experimental data [19] and [131]. The aforesaid is illustrated in fig. 219.

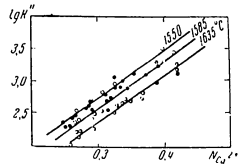

Fig. 219. Effect of the ionic fraction of calcium on the magnitude of K" in equation (VIII, 220).

For the first time a theoretical computation of the activity coefficients for oxides in slag was made by Kozheurov who took into account the difference in interaction of the simplest monatomic ions with oxygen [136]. His method is suited for the simplest molecular form of recording reaction equations, viz,

$$2P_{(met)} + 5FeO_{(sl)} = P_2O_{5(sl)} + 5Fe_{(met)}. \qquad \text{(VIII, 221)}$$

Consequently the expression for the equilibrium constant assumes the aspect of

$$K_P = \frac{x^5_P}{[\%\,P]^2 . x^5_{Fe}} \cdot \frac{\gamma^5_P}{\gamma^5_{Fe}} = K'_P \frac{\gamma^5_P}{\gamma^5_{Fe}}, \qquad \text{(VIII, 222)}$$

where x_i stands for the ionic fractions of the simplest cations.

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The activity coefficients γ_i are being calculated from the equations recorded earlier (page 343). In particular, for 1600°C temperature

$$\lg \gamma_{FeO} = 1{,}17\, x_{Mn} x_{Si} + 3{,}15 (x_{Ca} + x_{Mg}) x_{Si} + \\ + 5{,}6\, x_{Ca} x_P, \qquad \text{(VIII, 223)}$$

$$\lg \gamma_P \quad \lg \gamma_{FeO} - 5{,}6\, x_{Ca}. \qquad \text{(VIII, 224)}$$

The extent to which the equilibrium constant value thus calculated is constant, may be judged from table 32 which — for the sake of comparison — incorporates also the values determined per formula (VIII, 218). The equilibrium compositions of metal and slag are taken from the experimental material [131].

Reverting now to the influence of temperature, we see that, unlike desulfurization, the equilibrium distribution of phosphorus is very sensitive to any change in this factor. All equations recorded above indicate that metal dephosphorization declines with increasing temperature.

This is corroborated not only by laboratory tests but also by certain practical methods pertaining to the introduction of an oxidizing period in open-hearth heats.

Indeed, by using a special charging procedure it is possible to assure an early formation of sufficiently basic and ferrous slags at relatively moderate temperature.

Since the temperature grows unavoidably with the melting of the charge, this worsening of dephosphorization conditions must be offset by CaO additions. Quite frequently this is achieved automatically since the solubility of calcium oxide waxes with temperature.

On the basis of these considerations, Umrikhin, in a number of articles [129], [132], has described the effective methods of phosphorus elimination which permit one to reduce substantially the oxidizing period of heats.

To assure phosphorus removal in depth the so-called thermal shock technique was sometimes practiced in the past. A comparatively large quantity of ore and lime was introduced into the steel bath to cool off the metal while the gas was being cut off during the period of slagging [128]. This obsolete method is cited here only to illustrate the beneficial influence of a certain temperature drop on the process of dephosphorization.

THE SITE OF REACTION DEVELOPMENT.

The inference is often made in the technical literature dealing with the description of dephosphorization process that it develops within the volume of metal. It is considered, for instance, that ferrous oxide dissolves in metal first and then oxidizes the phosphorus which is present there up to P_2O_5 or even up to $3FeO \cdot P_2O_5$, whereupon these polyatomic molecules pass into slag where they react with CaO [61], [63], [82], [131].

Table 32. Equilibrium Constant of the Dephosphorization Reaction

Composition of metal, %		Composition of slag, %							t, °C	$(K_P)^{1/5}$	$K_P^{1/5}$	$K_P^{1/5}$ as per [131]
Mn	P	O	CaO	SiO_2	FeO	Fe_2O_3	MgO	P_2O_5	MnO				
—	0,016	0,156	24,21	9,90	48,48	7,34	5,29	4,02	—	1594	3,06	0,506	80,6
—	0,083	0,165	29,94	22,24	24,34	2,99	11,13	8,27	—	1608	4,53	0,432	78,8
0,083	0,049	0,067	35,52	27,72	12,87	2,16	9,77	3,55	7,68	1590	7,68	0,519	120,3
0,146	0,096	0,123	10,89	2,36	51,78	5,22	2,90	2,09	23,61	1598	1,07	0,490	19,8
0,212	0,111	0,082	39,94	15,38	10,59	1,77	5,23	16,09	10,60	1590	12,0	0,528	90,6
0,176	0,153	0,080	33,62	20,14	13,05	1,92	9,27	10,94	11,71	1594	7,5	0,565	74,0
0,124	0,029	0,086	37,78	8,04	5,14	3,99	10,91	8,70	—	1605	7,25	0,436	66,7
—	0,152	0,103	40,55	10,76	10,66	1,12	9,64	16,05	1,66	1590	10,80	0,465	102,0

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It is stated, in particular, that the removal of phosphorus "probably proceeds through the formation in metal of iron phosphate $Fe_3P_2O_8$ from which ferrous oxide is being expelled in slag by lime" [137].

However, such a reaction course is highly impeded by a relatively considerable disengagement of phosphorus and oxygen stoms in the metal phase, as a result of which the emergence of such complex particles as phosphates becomes possible only through gradual compounding of complexes.

Furthermore, the size of the P_2O_5 and $Fe_3P_2O_8$ particles is sufficiently large for their appearance to cause a powerful distortion in the arrangement of the neighboring atoms in metal. Moreover, the latter under certain conditions could destroy the phosphate anion.

This circumstance develops, in particular, from the fact of partial reduction of phosphates by pure iron.

Finally, the volume progress of the reaction surveyed is related to the formation stage of a new phase (P_2O_5 or $Fe_3P_2O_8$) within the metal. The low rate of the new phase formation can considerably retard the development of the process.

Experiments show [116], however, that the dephosphorization reaction proper progresses fairly rapidly. For this reason it seems more probable that its development takes place predominantly not within the steel bath, but rather along the metal-slag interface.

The fact of surface phosphorus activity speaks in favor of this theory. Actually it was established by a number of measurements that phosphorus reduces substantially the interphase tension of iron at the boundary with slag [138]. Large concentrations of phosphorus atoms, and possibly also those of oxygen, in the surface layer facilitate the formation of PO_4^{3-} anions here by means of successive addition of oxygen anions to the particle of phosphorus.

This is also enhanced by the fact that the surface of metal is negatively charged [138], i.e., containing an excess of electrons.

The emerging PO_4^{3-} ion passes directly into slag, a fact which eliminates the slow stage of the new phase formation.

So far there are no other data permitting one to judge the mechanism of the process of dephosphorization. Further investigations in this direction are very essential.

ON THE EX-FURNACE REMOVAL OF PHOSPHORUS.

In conclusion, a few words should be said with regard to the process of ex-furnace dephosphorization of metal of which the Soviet Union is the originator. It is based on the development of the same reaction as in furnaces. Consequently, ore (iron oxides) and calcium oxide are the most important components of the mixtures. Moreover, to assure a sufficiently

rapid progress of the process in the conditions of dropping temperature, non-viscous slag and a fairly large area of contact of the reacting phases are prerequisite. To effect a drop of the melting point of slag CaF_2 is sometimes introduced into the mixture.

Thus, for instance, Sokolovsky [139] describes a method of Bessemer metal dephosphorization by a synthetic mixture of the following composition: 50% CaO, 30% Fe_2O_3 and 20% CaF_2. Its quantity constituted 3% by weight of metal. Upon treatment the concentration of phosphorus sank from 0.10 to 0.02-0.04%, while the final slag contained 45% CaO, 14% (FeO + Fe_2O_3), 15-20% SiO_2, 8-10% MnO, 4-6% Al_2O_3, and 4-6% P_2O_5.

A study of Bessemer steel dephosphorization by basic slag was carried out in semi-industrial and industriel conditions by the Khar'kov Institute of Metals. As reported by Kostyuchenko [140] the tests, conducted in 1933, showed that the addition of medium carbon rail steel into liquid synthetic slag (5-7% SiO_2, 45-48% CaO, 23-25% (Fe + Fe_2O_3), 9-12% MnO, 4-6% MgO, 8-10% Al_2O_3) reduces phosphorus contents by 70% (up to 0.035% P), diminishes the proportion of non-metallic inclusions, and improves the mechanical properties of metal.

4. DECARBONIZATION PROCESS.

The process of decarbonization is of extremely great importance for the metallurgy of steel. During its oxidation carbon concentration in metal is not only reduced to the required level; other equally important phenomena are connected with this process. Cited among them should be, for instance, the intensification of heat transfer, acceleration of the transport of reagents, equalization of the compositions of metal and slag, partial outgassing of the bath, facilitation of the removal of non-metallic inclusions, and so on.

In spite of a great number of investigations, the process in question is still insufficiently well studied. This is primarily due to the extreme complexity of the problem. The limited space available does not permit us to make a critical evaluation in this chapter of the entire material accumulated in literature. The subsequent discussion will be confined only to the process of decarbonization in open-hearth furnace.

During the initial period of charge melting, lumps of metal are in direct contact with the oxidizing furnace gases. Moreover, along with a partial burnout of carbon there occurs the formation of ferrous slag. The latter reacts intensively with metal and saturates it with oxygen which oxidizes carbon.

The direct contact between the metal and furnace gas stops after the metal is completely covered with slag. This contact may again be resumed as a result of the exposure of molten metal by a gas stream (near the furnace end), or, which is even more essential, in consequence of the ejection of its drops (beads) by the bubbles of the evolving carbon monoxide. In spite of all this, the oxidation of metal by furnace gases through the

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slag layer still constitutes the dominating process.

Frequently, in order to increase interaction, iron ore is added to slag which increases sharply its oxidizing capacity. The peculiarities of this so-called ore boil will not be discussed below, neither shall we consider the problems pertaining to the direct reaction of metal carbon with furnace gases.

Our principal attention in this chapter will be confined to the analysis of pure ebullition without ore, i.e., the process of oxygen transition from gaseous phase into metal through a layer of liquid slag.

OUTLINE OF THE CARBON OXIDATION PROCESS.

The triphase gas - slag - metal system is not in equilibrium in the conditions of steel furnace. The chemical potential of oxygen happens to be the greatest in the first phase and the lowest in the third. In view of this fact, oxygen passes from furnace gases into slag and therefrom into metal.

Chemical adsorption of oxygen[1] takes place at the gas-slag surface boundary (I)

$$O_{2\,(gas)} = 2\,O_{(ads)}, \qquad \text{(VIII, 225)}$$

which is accompanied by oxygen ionization and oxidation of the iron cations[2]

$$O_{(ads)} + 2\,Fe^{2+}_{(sl)} + 3\,O^{2-}_{(sl)} \rightleftharpoons 2\,FeO^{-}_{2\,(sl)}. \qquad \text{(VIII, 226)}$$

These apparently inseparable stages lead to the enrichment of the surface slag layer with FeO^{-}_{2} ions[3] and deplete it of Fe^{2+} cations and O^{2-} anions.

The increasing concentration of FeO^{-}_{2} ions causes their diffusion throughout the slag towards metal.

It is greatly accelerated by convection drifts caused by the rising CO bubbles, by the dropping beads of metal, by the inhomogeneity of the temperature field, and by other factors.

On reaching interface (II) of slag and metal the trivalent iron anions

1) Or oxygen bearing gases, e.g., CO_2, H_2O, as this occurs during oxidation of solid iron (see part I, page 374).

2) No data are available with regard to the dissolution of atomic or molecular oxygen.

3) The formula of the trivalent iron anion is tentative; it may also be expressed in a different way.

are being reduced

$$2\,FeO^{-}_{2} + Fe_{(met)} = 3\,Fe^{2+}_{(sl)} + 4\,O^{2-}_{(sl)}, \qquad \text{(VIII, 227)}$$

while the ions Fe^{2+} and O^{2-} pass partially into metal

$$Fe^{2+}_{(sl)} + O^{2-}_{(sl)} = Fe_{(met)} + O_{(met)}. \qquad \text{(VIII, 228)}$$

In consequence of reactions (VIII, 227) and (VIII, 228) the contents of divalent iron and O^{2-} anions increases here causing their simultaneous migration toward interface (I) of slag with gas. In this sense it is possible to speak of a ferrous oxide flow.

The oxygen atoms, after penetration into metal, will be moved through diffusion and convection channels to the reaction surface. Since the existence of CO molecules in liquid iron is highly improbable, then interaction between carbon and oxygen must occur only at the metal-bubble interface.

$$C_{(met)} + O_{(met)} = CO_{(bub)}. \qquad \text{(VIII, 229)}$$

Reaction (VIII, 229) is, therefore, not homogeneous but heterogeneous. It is not collison of carbon and oxygen atoms within the metal volume that is required for its realization, but rather their diffusion and convection flow towards the surface of the bubbles. Here, i.e., at these interfaces, occurs the chemical reaction and the desorption (i.e., the release connected with the surface reaction) of carbon and oxygen atoms in the form of CO molecules.

Finally, the presence of carbon monoxide bubbles is essential for the development of the process (VIII, 229). Their formation represents a very important stage of the process. Since the obstacles to the formation of a new gaseous phase within the metal are too great, the CO bubbles usually originate at the metal-hearth interface (III).

Yet, in individual cases the so-called surface boil may take place, when the gas bubbles form at the metal-slag surface boundary (II).

This, in brief, is the outline of the process of decarbonization. As a whole it could be reduced to the absorption of oxygen and evolution of CO. According to Karnaukhov's graphic simile, the process could be likened to breathing - the bath inhales the oxygen of furnace gases and exhales carbon monoxide into them.

A detailed analysis of carbon combustion shows that this is a very complex problem. The foregoing, as a matter of fact, enables the following stages to be outlined:

1. Transfer of oxygen from gas to metal.

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a) Passage of oxygen from gas to slag.
b) Its diffusion towards metal.
c) Transfer of oxygen from slag to metal.

2. Interaction of carbon and oxygen in metal.

a) Diffusion of carbon and oxygen to the reaction surface.
b) Chemical desorption of C and O atoms in the form of CO molecules into the bubble.

3. Formation of the bubbles and their passage through metal into slag.

An effort has been made below to provide a detailed analysis for each of the enumerated stages.

PASSAGE OF OXYGEN FROM GAS TO METAL.

Equilibrium in Purely Ferrous Slags.

If the stages of adsorption (VIII, 225) and oxygen ionization (VIII, 226) are not separated one from another, then the passage of oxygen from gas to slag could be represented, for instance, by the following stoichiometric formula

$$O_{2\,(gas)} + 4\,Fe^{2+}_{(sl)} + 6\,O^{2-}_{(sl)} = 4\,FeO^{-}_{2\,(sl)}. \qquad \text{(VIII, 230)}$$

The equilibrium of this reaction was repeatedly studied experimentally. In particular, it was investigated [141] over the interval of temperatures from 1400 to 1600°C for pure ferrous slags (FeO + Fe_2O_3) and the gaseous phase consisting of CO and CO_2

$$2\,FeO_{(sl)} + CO_{2\,(gas)} = Fe_2O_{3\,(sl)} + CO_{(gas)}. \qquad \text{(VIII, 231)}$$

The activities of FeO in the melt were calculated on the basis of these data.

The interpretation of these results from the positions of the ionic theory was made in the assumption [142] that trivalent iron is present in slag both in the form of $Fe_2O_5^{4-}$ anion and in that of Fe^{3+} cation. The selection of the anion was motivated thereby [142] by the presence of calcium ferrite $2CaO \cdot Fe_2O_3$ in solidified slags.

It was further assumed that at small Fe_2O_3 contents the reaction may be schematically represented as follows

$$2\,Fe^{2+}_{(sl)} + 4\,O^{2-}_{(sl)} + CO_{2\,(gas)} = Fe_2O_5^{4-}{}_{(sl)} + CO_{(gas)}, \qquad \text{(VIII, 232)}$$

with the equilibrium constant appearing as

$$K_1 = \frac{p_{CO}}{p_{CO_2}} \cdot \frac{a_{Fe_2O_5^{4-}}}{a^2_{Fe^{2+}} \cdot a^4_{O^{2-}}}. \qquad \text{(VIII, 233)}$$

It turned out that the activities are close to ionic fractions calculated on the basis of the theory of perfect solutions if the ratios of the atomic fractions of oxygen N_O and iron N_F are not too large, namely, not exceeding 1.15. In other words, the equilibrium constant K_1 remains more or less unchanged when the activities are replaced by ionic fractions

$$K \cong \frac{p_{CO}}{p_{CO_2}} \cdot \frac{N_{Fe_2O_5^{4-}}}{N^4_{O^{2-}}} = \frac{p_{CO}}{p_{CO_2}} \cdot \frac{(1 - N_{O^{2-}})}{N^4_{O^{2-}}}. \qquad \text{(VIII, 234)}$$

The foregoing is illustrated by the data from table 33.

On the contrary, when Fe_2O_3 concentrations are large, deviations arise which are attributable [142] to partial dissociation of the $Fe_2O_5^{4-}$ anion

$$Fe_2O_5^{4-}{}_{(sl)} = 2\,Fe^{3+}_{(sl)} + 5\,O^{2-}_{(sl)}. \qquad \text{(VIII, 235)}$$

The dissociation is caused by a relative decrease of the concentration of free O^{2-} ions. In these conditions the ionic fraction is no longer equal to unity, because a second cation — Fe^{3+} — appears in the melt.

Table 33. Equilibrium of reaction (VIII, 232) for small percentages of Fe_2O_3

t, °C	N_O/N_{Fe} (test)	P_{CO_2}/P_{CO} (test)	$N_{Fe_2O_5^{4-}}$ (computed)	$N_{O^{2-}}$ (computed)	$a_{O^{2-}}$ (computed)	K_1 (test)
1500	1.04	0.384	0.046	0.954	0.954	0.145
	1.07	0.886	0.088	0.912	0.912	0.144
	1.10	1.893	0.143	0.857	0.855	0.140
	1.15	6.60	0.272	0.728	0.791	0.147
						0.144 (average)
1600	1.04	0.425	0.046	0.954	0.954	0.131
	1.07	0.952	0.088	0.912	0.912	0.134
	1.10	1.97	0.857	0.143	0.857	0.135
	1.15	6.48	0.272	0.728	0.740	0.149
						0.133 (average)

Still assuming the activity coefficients of O^{2-} and $Fe_2O_5^{4-}$ anions to

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be equal to unity, we record equation (VIII, 233) in a somewhat different form

$$K_1 = \frac{p_{CO}}{p_{CO_2}} \cdot \frac{(1 - N_{O^{2-}})}{a^{n}_{FeO} \cdot N^{2}_{O^{2-}}}. \qquad \text{(VIII, 236)}$$

Here

$$a_{FeO} = a_{Fe^{2+}} \cdot a_{O^{2-}}. \qquad \text{(VIII, 237)}$$

By taking the value of K_1 from table 33, and the P_{CO}/P_{CO_2} ratio as well as the activity of FeO from experimental data, we find from equation (VIII, 236) the magnitude of $N_{O^{2-}}$, and from it also that of $N_{Fe_2O_5^{4-}}$. The ensuing results are listed in table 34.

Assuming

$$a_{O^{2-}} = N_{O^{2-}}, \qquad \text{(VIII, 238)}$$

we determine $a_{Fe^{2+}}$ on the basis of equation (VIII, 237) and the experimental values of a_{FeO}.

In order to calculate $N_{Fe^{2+}}$ and $N_{Fe^{3+}}$, quantities $n_{Fe^{2+}}$ and $n_{Fe^{3+}}$ are introduced which designate the number of the cation moles per one mole of all anions. Thereby

$$N_{Fe^{2+}} = \frac{n_{Fe^{2+}}}{n_{Fe^{2+}} + n_{Fe^{3+}}}. \qquad \text{(VIII, 239)}$$

Then a material balance equation is composed

$$\frac{N_{O^{2-}} + 5N_{Fe_2O_5^{4-}}}{2N_{Fe_2O_5^{4-}} + n_{Fe^{2+}} + n_{Fe^{3+}}} = \frac{N_O}{N_{Fe}} \qquad \text{(VIII, 240)}$$

as well as that for slag electroneutrality

$$2n_{Fe^{2+}} + 3n_{Fe^{3+}} = 2N_{O^{2-}} + 4N_{Fe_2O_5^{4-}}, \qquad \text{(VIII, 241)}$$

from which

$$N_{Fe^{2+}} \quad \text{и} \quad N_{Fe^{3+}}.$$

are being determined.

As it transpires from table 34, the activity coefficient of divalent iron ions approaches unity. In other words, the theory of perfect ionic solutions remains to be valid in this case too.

Table 34. Equilibrium of reaction (VIII, 232) for increased Fe_2O_3 contents at 1600°C and $K_1 = 0.133$.

N_O/N_{Fe} (test)	P_{CO_2}/P_{CO} (test)	a_{FeO} (test)	$N_{O^{2-}}$ (computed)	$N_{Fe_2O_5^{4-}}$ (computed)	$N_{Fe^{2+}}$ (computed)	$a_{Fe^{2+}}$ (computed)	$\gamma_{Fe^{2+}}$ (test)
1,20	20,0	0,607	0,622	0,378	0,939	0,976	1,04
1,25	63,1	0,468	0,514	0,486	0,851	0,911	1,07
1,30	223,9	0,332	0,421	0,579	0,733	0,788	1,07
1,33	549,5	0,248	0,374	0,626	0,638	0,664	1,04
1,34	668,3	0,233	0,363	0,637	0,617	0,642	1,04
1,37	1660,0	0,169	0,327	0,673	0,520	0,517	0,99

The exposed interpretation does not provoke any particular questions, but it calls for a better argumentation of its initial positions.

In particular, the presence of trivalent iron in the form of anions with a small charge-to-radius ratio follows from the fact of the decreasing surface tension of FeO as a result of Fe_2O_3 addition, and that of the expulsion of the latter from the melt through introduction of SiO_2.

These conditions are satisfied, for instance, by FeO_2^- and $Fe_2O_5^{4-}$ anions. It is also obvious that the Fe^{2+} cation is capable of deforming strongly the above anions and even to destroy them, while liberating the ion of trivalent iron Fe^{3+}. Let it also be remembered that Fe^{2+} removes O^{2-} even from more stable silicon cations breaking up thereby the anions of SiO_4^{4-}.

The defect of the reported interpretation consists in the insistent desire at all cost to select such form of anion as would assure the applicability of the ideal law of mass action. It was mentioned earlier that this is not always the right avenue, since the activities of ions in the melt must not at all coincide with their concentrations.

Extremely significant in this connection is the fact that absolutely different conclusions were reached by Kozheurov [143]. While processing the same experimental material relative to the equilibrium of FeO + Fe_2O_3 with CO + CO_2 [141], he found that the equilibrium constant of reaction (VIII, 231) may be represented by the following unusual equation

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$$K = \frac{p_{CO_2}}{p_{CO}} \cdot e^{\frac{-23200}{RT}(x_2^2 - x_1^2)}, \qquad \text{(VIII, 242)}$$

in which x_1 and x_2 are the ionic fractions of Fe^{2+} and Fe^{3+} in slag.

If one assumes that the melt represents a regular solution of Fe^{3+} and Fe^{2+} cations combined with O^{2-} anion, then the equation (VIII, 242) will not incorporate the activities of ions but only the coefficients of their activities. In other words, the deviation from the ideal law of mass action is extremely high here, since the determining role is not played by concentrations (replacing the activities) but by their correction factors.

Kozheurov explains the obtained regularities by a continuous exchange of electrons between the Fe^{2+} and Fe^{3+} ions "as a result of which the average charge of all cations becomes identical", while the communal entropy of mixing vanishes. To what extent this interpretation is correct it is difficult to say. At any rate it demands further experimental corroboration.

Effect of Slag Basicity.

When the composition of the gaseous phase is fixed and the temperature is constant, the relative concentration of Fe_2O_3 defined by expression

$$M_{Fe_2O_3} = \frac{(Fe_2O_3)}{(Fe_2O_3) + (FeO)} \cdot 100\%, \qquad \text{(VIII, 243)}$$

increases, as shown by test, with growing CaO contents and diminishing percentage of SiO_2.

Fig. 220 provides a ternary diagram $CaO-SiO_2-(FeO + Fe_2O_3)$, which shows [147] the lines of equal values of $M_{Fe_2O_3}$. The experimental data relate to the equilibrium of slag with air at 1592°C.

The recorded curves differ little from straight-lines, a fact which suggests the existence of a linear relationship between the concentrations of CaO and SiO_2. Indeed it may be seen from fig. 221 that the ratio for the straight-line $\beta\omega$ is constant

$$\frac{(SiO_2)}{y} = \alpha = \text{const.} \qquad \text{(VIII, 244)}$$

Since

$$y = \beta - [(FeO) + (Fe_2O_3)] \qquad \text{(VIII, 245)}$$

and

$$(CaO) + (SiO_2) + (FeO) + (Fe_2O_3) = 100, \qquad \text{(VIII, 246)}$$

then

$$(CaO) - \frac{(1-\alpha)}{\alpha} \cdot (SiO_2) = 100 - \beta. \qquad \text{(VIII, 247)}$$

In the similar manner for the straight-line $\beta_1\omega_1$

$$(SiO_2) - \frac{(1-\alpha_1)}{\alpha_1} \cdot (CaO) = 100 - \beta_1, \qquad \text{(VIII, 248)}$$

where

$$\alpha_1 = \frac{(CaO)}{y_1}. \qquad \text{(VIII, 249)}$$

The fact that the straight-lines in fig. 220 are almost parallel evidences a sufficient constancy of coefficient α. It also transpires from the diagram that $\alpha > 0.6$.

We shall see now how the concentration of oxygen ions ($N_{O^{2-}}$) varies along such a line. For this purpose let us consider only sufficiently basic slags in which

$$\frac{(CaO) + (FeO)}{(SiO_2) + (Fe_2O_3)} > 2. \qquad \text{(VIII, 250)}$$

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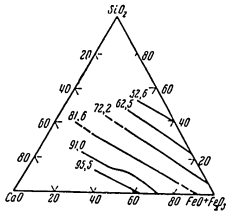

Fig. 220. Relative contents of ferric oxide $\left[\frac{Fe_2O_3 \cdot 100}{FeO + Fe_2O_3}\%\right]$ in the system CaO – SiO_2 – (FeO + Fe_2O_3) at equilibrium with air at 1592°C

From the invariability of $M_{Fe_2O_3}$ it follows that M' is constant, i.e.,

$$M' = \frac{(Fe_2O_3)}{(FeO)} = \text{const.} \qquad \text{(VIII, 251)}$$

In conjunction with equation (VIII, 246) this yields

$$(CaO) + (SiO_2) + (FeO)(1 + M') = 100, \qquad \text{(VIII, 252)}$$

whence

$$N_{O^{2-}} = (CaO) + (FeO) - 2(Fe_2O_3) - 2(SiO_2) = \qquad \text{(VIII, 253)}$$
$$= \frac{3}{1+M'}[M'(CaO) - (SiO_2)] + \frac{1-2M'}{1-M'} \cdot 100.$$

Taking into account the linear relationship (VIII, 247) between (CaO) and (SiO_2) which is characteristic for these straight-lines, we have

$$N_{O^{2-}} = \frac{3}{1+M'}\left[M'(CaO) - \frac{\alpha}{1-\alpha}(CaO)\right] + \qquad \text{(VIII, 254)}$$
$$+ \frac{3(100-\beta)}{(1+M')(1-\alpha)} + \frac{1-2M'}{1+M'} \cdot 100.$$

Since for basic slags the value of M' is always larger than unity and

grows from one straight-line to another with increasing (CaO), while the quantity $\frac{\alpha}{1-\alpha}$ is smaller than unity and decreases, then the concentration of oxygen ions cannot be constant along each of the lines of equal $M_{Fe_2O_3}$ values. It sinks with the decrease of calcium oxide percentage and with the growth of ferrous oxide contents. In other words, it transpires from the experimental data that $N_{O^{2-}}$ is variable when M' is constant.

Let us now revert to the stoichiometric patterns of reactions (VIII, 230) and (VIII, 232) to find out the measure to which they are capable of explaining these facts. The equilibrium constant for the first of them may be recorded as

$$K = \frac{a^4_{FeO_2^-}}{a^4_{Fe^{2+}} \cdot a^6_{O^{2-}} \cdot p_{O_2}}, \qquad \text{(VIII, 255)}$$

whereupon

$$M' = \frac{N_{FeO_2^-}}{N_{Fe^{2+}}} = K^{1/4} \cdot p_{O_2}^{1/4} \cdot N'^{3/2}_{O^{2-}} \cdot \frac{\gamma^{3/2}_{Fe^{2+}} \cdot \gamma^{3/2}_{O^{2-}}}{\gamma_{FeO_2^-}}. \qquad \text{(VIII, 256)}$$

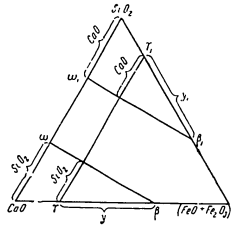

Fig. 221. Schematic diagram of the compositions of the system CaO – SiO_2 – (FeO + Fe_2O_3).

It is known that the product $\gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}}$ changes strongly with the concentration of O^{2-} ions. As a matter of fact, this relationship could be represented by the following empirical equation

$$\gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}} = \frac{1}{N'^{3/2}_{O^{2-}}}. \qquad \text{(VIII, 257)}$$

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Then

$$M' = (K \cdot p_{O_2})^{\frac{1}{4}} \cdot \frac{\gamma_{O^{2-}}}{\gamma_{FeO_2}} . \qquad \text{(VIII, 258)}$$

The equation produced is incapable, it seems to us, to explain the observed (see fig. 220) increase of $M_{Fe_2O_3}$ and M' with growing CaO contents when the percentage of FeO is unchanged. Indeed, the quantity (K_{p_O}) is constant, whereas the activity coefficients of O^{2-} and FeO_2^- anions must increase along with the concentration of CaO, since the interaction energy with Ca^{2+} cation is smaller than with the ion Fe^{2+}. To the extent that the square root is extracted from $\gamma_{O^{2-}}$, the numerator would hardly grow faster than the denominator. Therefore, in spite of the experimental data, M' does not increase with growing CaO contents.

If, on the contrary, formula (VIII, 232) is to be utilized, then, according to equation (VIII, 233) we obtain

$$M'' = \frac{N_{Fe_2O_5^{4-}}}{N_{Fe^{2+}}} = K_1 \frac{p_{CO_2}}{p_{CO}} N_{O^{2-}}^4 \cdot N_{Fe^{2+}} \cdot \frac{\gamma_{Fe^{2+}}^2 \cdot \gamma_{O^{2-}}^4}{\gamma_{Fe_2O_5^{4-}}} . \qquad \text{(VIII, 259)}$$

Taking equation (VIII, 257) into consideration, we have

$$M'' = K_1 \frac{p_{CO_2}}{p_{CO}} N_{O^{2-}} \cdot N_{Fe^{2+}} \cdot \frac{\gamma_{O^{2-}}^2}{\gamma_{Fe_2O_5^{4-}}} . \qquad \text{(VIII, 260)}$$

The latter expression is in better accord with the experimental values. Actually, when the concentration of FeO is given, i.e., with $N_{Fe^{2+}}$ = const., the growth of $N_{O^{2-}}$, i.e., (CaO), leads to increasing M''. It is natural to think that the square of the activity coefficient $\gamma_{O^{2-}}$ augments together with $N_{Ca^{2+}}$ somewhat faster than the first power of quantity $\gamma_{Fe_2O_5^{4-}}$.

Moreover, equation (VIII, 260) is capable to provide an explanation, at least qualitatively, for the fact that for each line of equal $M_{Fe_2O_3}$ and M'' values the concentration $N_{O^{2-}}$ drops when the contents of FeO, i.e., $N_{Fe^{2+}}$, is growing. It is possible to presume that the decline of the factors $N_{O^{2-}}$ and $\frac{\gamma_{Fe^{2+}}^2}{\gamma_{Fe_2O_5^{4-}}}$ compensated by an increase of the magnitude $N_{Fe^{2+}}$.

On the Kinetics of Oxygen Migration from Gas to Metal.

As far as we know, the kinetics of the penetration by oxygen of the liquid slag-gas boundary has never been experimentally studied at all. In spite of this, it seems possible to assume that under normal smelting conditions the given stage does not limit the development of the process of carbon burn-out.

As a matter of fact had the process of oxygen transmission from gas been slow, the Fe_2O_3 contents in slag would have been very small and evenly distributed along the entire cross-section of the layer. This, however, is not confirmed by tests.

Thus, Medzhibozhsky [145] using a ladle of special design took samples from various slag levels. Among other things, he was able to establish that when the metal (0.09% and 0.22% Mn) is calm, the concentrations of Fe_2O_3 in slag are high enough and change regularly with height (table 35).

Table 35. Fe_2O_3 contents along the height of the slag layer.

Layer	Concentration, %		
	FeO	Fe_2O_3	$M_{Fe_2O_3}$
Upper	8.48	8.68	50.5
Medium	11.75	5.03	30.0
Lower	13.63	2.07	13.2

The inhomogeneity of the slag composition in height is also noted by Umrikhin. According to his data [146], the difference in Fe_2O_3 contents in the surface layer of slag and in the intermediate horizons comprises 0.2 - 4%. The higher values of the Fe_2O_3 concentration drop reported by other investigators are to be attributed, he thinks, to disregard of the macro-inhomogeneity of slag.

The kinetically fairly well studied process of solid iron oxidation by gaseous phase can serve as another confirmation of rapid oxygen assimilation by slag. Experiments show that in this case the passage of oxygen from gas into scale ordinarily does not limit the process as a whole.

PASSAGE OF OXYGEN FROM SLAG TO METAL.

Two processes take place at the boundary of slag with metal: the reduction of trivalent iron to divalent, and the passage of the latter into steel together with the anions of oxygen. Up to the present time only the equilibria of these reactions were experimentally investigated.

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Equilibria with Purely Ferrous Slags.

Let us first consider reaction (VIII, 228)

$$Fe^{2+}_{(sl.)} + O^{2-}_{(sl.)} = Fe_{(met)} + O_{(met)}.$$

It was investigated by a number of authors. They all agreed that the solubility of oxygen in liquid metal increases with temperature.

Let it be noted here, that Ageyev [147] is well justified in his criticism of the old formulas proposed by Herty

$$[O]_{max} = 0{,}1475 \cdot 10^{-2} t - 2{,}058, \qquad \text{(VIII, 261)}$$

and by Koerber and Oelsen

$$[O]_{max} = 0{,}131 \cdot 10^{-2} t - 1{,}77, \qquad \text{(VIII, 262)}$$

for their linear and not exponential character.

In more recent works measurements were made with greater precautions. For instance, to avoid errors which might arise in consequence of a contact between pure ferrous slag with the refractory lining, a rotary crucible was used in which iron oxides were placed into a depression formed by the metal [148]. On the basis of these data a temperature dependence was proposed [142] for equilibrium (VIII, 228)

$$\lg L = \lg \frac{a_{FeO}}{[\%\ O]} = \lg \frac{a_{Fe^{2+}} \cdot a_{O^{2-}}}{[\%\ O]} = \frac{6000}{T} - 2{,}57. \qquad \text{(VIII, 263)}$$

The solubility of oxygen in iron covered by a layer of Fe_xO_y, at $a_{FeO} = 1$ and different temperatures, calculated from equation (VIII, 263), amounts to

t,°C	1540	1580	1620	1660	1700	1740
[% O]	0,1822	0,2148	0,2512	0,2927	0,3381	0,3885

From expression (VIII, 263) it also follows that the heat of ferrous oxide transfer from slag to metal is great comprising 27,450 cal per mole. It appears to be approaching the heat absorbed during the solution of gaseous oxygen ($\frac{1}{2} O_2$) in liquid iron - 27,930 cal per g.-atom of oxygen [149]. This fact points to the existence of considerable energy impediments

arising during the passage of O^{2-} and Fe^{2+} ions across the slag-metal boundary.

It is important here to underscore the constancy of the activity coefficient of oxygen dissolved in liquid iron. It apparently is equal to unity, which not only follows from the diluteness of the O solutions in Fe, but is also supported by direct experimental evidence. Indeed, as mentioned in chapter VII, there exists a direct proportionality between [%O] and the P_{H_2O} to P_{H_2} ratio, which permits one to assume that $\gamma_O = 1$.

Thus, oxygen in liquid iron can be found only in states of energy equivalence, which do not mutually influence one another. Hence, there is hardly any sense in speaking of the presence in metal of two forms of oxygen - the free O and that combined in FeO.

In passing over to trivalent iron, let us remark that its concentration drops considerably when equilibrium is attained between slag and metal. For reaction

$$3Fe^{2+}_{(sl.)} + 5O^{2-}_{(sl.)} = Fe_{(met)} + Fe_2O^{4-}_{5\,(sl.)} \qquad \text{(VIII, 264)}$$

an estimate was made [142], on the basis of the data for pure ferrous slags, of the equilibrium constant

$$K_2 = \frac{a_{Fe_2O_5^{4-}}}{a^3_{Fe^{2+}} \cdot a^5_{O^{2-}}}. \qquad \text{(VIII, 265)}$$

It proved to be equal to 0.0255 at 1600° and 0.0395 at 1400°C, i.e., being 4-5 times inferior to the values pertaining to the slag-gas interface.

Effect of Calcium Oxide and Silica.

A lowering of oxygen contents in metal and an increase of $Fe_2O_5^{4-}$ concentration is to be observed upon addition of calcium or magnesium oxides into pure ferrous slag. To put it in another way, both equilibria (VIII, 228) and (VIII, 264) are being shifted to the right.

According to equation (VIII, 263)

$$a_{FeO} = a_{Fe^{2+}} \cdot a_{O^{2-}} = L\,[\%\ O], \qquad \text{(VIII, 266)}$$

i.e., the magnitude of [%O] constitutes the measure of the activity of ferrous oxide in slag.

With the aid of this fact it is possible to show that the introduction of CaO into slag practically does not affect the activity coefficient

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$\gamma^2_{FeO} = \gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}}$. It follows from the experimental data [142] that γ^2_{FeO} varies within the limits of 0.9 and 1.15 when about 60% FeO are replaced by CaO.

On the other hand, the activity coefficient of $Fe_2O_5^{4-}$ anion diminishes strongly with growing CaO contents and simultaneously dropping FeO concentration, as it may be seen from fig. 222. The recorded $\gamma_{Fe_2O_5^{4-}}$ values were calculated [142] from equation (VIII, 267) obtained by means of relationships (VIII, 265) and (VIII, 266)

$$K_3 = L'K_2 = \frac{N_{Fe_2O_5^{4-}} \cdot \gamma_{Fe_2O_5^{4-}}}{a_{Fe^{2+}} \cdot a^3_{O^{2-}} \cdot [\%\ O]^3}. \qquad \text{(VIII, 267)}$$

It was assumed thereby that the activity of Fe^{2+} is equal to its ionic fraction and the coefficient $\gamma_{O^{2-}}$ was consequently taken to be equal to γ^2_{FeO}. A strong drop of $\gamma_{Fe_2O_5^{4-}}$ with growing CaO percentage can, obviously, not be explained by simple increase of $Fe_2O_5^{4-}$ anion concentration. The absolute value of $N_{Fe_2O_5^{4-}}$ remains to be small. One should think that this fact is related to the micro-inhomogeneity of slag, and to the greater stability of $Fe_2O_5^{4-}$ anions in the presence of "weak" Ca^{2+} cations, than in the presence of "strong" Fe^{2+} cations.

A simultaneous addition of CaO and SiO_2 to pure ferrous slags (as contrasted with the introduction of CaO alone) sharply raises the activity coefficient of ferrous oxide. This was discussed in detail earlier (see Chapter VI). It was also emphasized there that the effect under consideration is caused by two types of cybotactic groups, on one of which predominant are the ions Ca^{2+} and SiO_4^{4-}, while Fe^{2+} and O^{2-} ions are prevalent in the other.

that no equilibrium could be achieved in these experiments at concentrations [%C] > 1%.

This deduction cannot be accepted though. The fact of the matter is that the growth of coefficient γ_C with the contents of carbon was also revealed by other authors [177] and by means of other methods [47] (see also part I of the present monograph).

In investigating industrial heats, Chufko was able to establish that for reactions (VIII, 288) and (VIII, 288'), i.e.,

$$C_{(melt)} + O_{(melt.)} = CO_{(gas)},$$
$$C_{(melt)} + FeO_{(sl)} = CO_{(gas)} + Fe_{(melt)}$$

the pressures of CO are different and they are greater for the second than for the first

$$p''_{CO} > p'_{CO}.$$

Only one fact transpires thereby that the system was not in a state of equilibrium. Yet he draws a conclusion to the effect that the activity coefficient of oxygen is independent of the concentration of carbon.

No more conclusive is his statement that from the totally unsubstantiated relationship

$$[\%\ C] = [\Sigma C] \cdot \gamma_C \qquad \text{(VIII, 314)}$$

it follows allegedly that the coefficient γ_C drops with the increase of total carbon concentration [210].

Little is conveyed by Baptizmansky's efforts to prove the constancy of γ_C and γ_O on the basis of Kinetic data (on the weak dependence of the rate of carbon burnout upon its contents in metal).

In a series of works by Samarin and co-authors, an attempt is made to explain the variability of coefficients γ_C and γ_O without resort to the hypothesis concerning the existence in molten metal of molecules of CO, Fe_2C, and so on. The point of departure here is constituted by the postulates developed by Temkin and Schwartzmann. According to the latter, the deviations from ideal solutions, observed in iron alloys, are caused mainly by spatial limitations in the arrangement of the atoms of the solute.

How the growth of coefficient γ_O with the concentration of carbon is explained from this point of view was described earlier.

In discussing the variation of coefficient γ_O Samarin and Schwartzman [182] observe that "oxygen, unlike carbon, does not dissolve in iron according to the intrusion pattern, and its solubility can therefore be

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$\gamma^2_{FeO} = \gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}}$. It follows from the experimental data [142] that γ^2_{FeO} varies within the limits of 0.9 and 1.15 when about 60% FeO are replaced by CaO.

On the other hand, the activity coefficient of $Fe_2O_5^{4-}$ anion diminishes strongly with growing CaO contents and simultaneously dropping FeO concentration, as it may be seen from fig. 222. The recorded $\gamma_{Fe_2O_5^{4-}}$ values were calculated [142] from equation (VIII, 267) obtained by means of relationships (VIII, 265) and (VIII, 266)

$$K_s = L^3 K_2 = \frac{N_{Fe_2O_5^{4-}} \cdot \gamma_{Fe_2O_5^{4-}}}{a_{Fe^{2+}} \cdot a^3_{O^{2-}} \cdot [\%\ O]^5}. \qquad \text{(VIII, 267)}$$

It was assumed thereby that the activity of Fe^{2+} is equal to its ionic fraction and the coefficient $\gamma_{O^{2-}}$ was consequently taken to be equal to γ^2_{FeO}. A strong drop of $\gamma_{Fe_2O_5^{4-}}$ with growing CaO percentage can, obviously, not be explained by simple increase of $Fe_2O_5^{4-}$ anion concentration. The absolute value of $N_{Fe_2O_5^{4-}}$ remains to be small. One should think that this fact is related to the micro-inhomogeneity of slag, and to the greater stability of $Fe_2O_5^{4-}$ anions in the presence of "weak" Ca^{2+} cations, than in the presence of "strong" Fe^{2+} cations.

A simultaneous addition of CaO and SiO_2 to pure ferrous slags (as contrasted with the introduction of CaO alone) sharply raises the activity coefficient of ferrous oxide. This was discussed in detail earlier (see Chapter VI). It was also emphasized there that the effect under consideration is caused by two types of cybotactic groups, on one of which predominant are the ions Ca^{2+} and SiO_4^{4-}, while Fe^{2+} and O^{2-} ions are prevalent in the other.

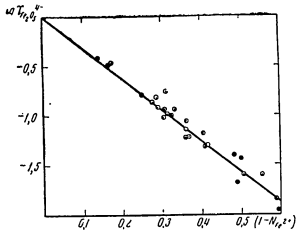

Fig. 222. Effect of the ionic fraction of iron $N_{Fe^{2+}}$ on the activity coefficient of the ferrite ion $Fe_2O_5^{4-}$.

Fig. 223 can be offered to serve as an additional illustration. It shows the drop of

$$L' = \frac{N_{Fe^{2+}} \cdot N_{O^{2-}}}{[\%\ O]}$$

with growing percentage of complex anions SiO_4^{4-} and PO_4^{3-} [105].

If one assumes the empirical equation

$$\gamma_{Fe^{2+}} \cdot \gamma_{O^{2-}} = \gamma^2_{FeO} = \frac{1}{N'^2_{O^{2-}}}, \qquad \text{(VIII, 268)}$$

to be valid, then the dependence of L

$$L = \frac{a_{Fe^{2+}} \cdot a_{O^{2-}}}{[\%\ O]} = \frac{N_{Fe^{2+}}}{[\%\ O]\, N'^2_{O^{2-}}} \qquad \text{(VIII, 269)}$$

on the temperature may be expressed [105] by the equation (fig. 224)

$$\lg L = \lg \frac{N_{Fe^{2+}}}{[\%\ O]\, N'^2_{O^{2-}}} = \frac{7000}{T} - 3{,}258. \qquad \text{(VIII, 270)}$$

The latter does not differ too much from expression (VIII, 263) in which the relationship between γ_{FeO} and $N_{O^{2-}}$ was not taken into account.

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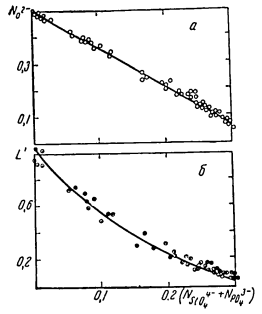

Fig. 223. Dependence of $N_{O^{2-}}$ (a) and L' (b) upon the contents of ($N_{SiO_4^{4-}}$ + $N_{PO_4^{3-}}$) at 1570-1640°C

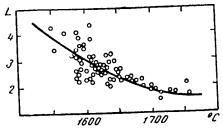

Fig. 224. Effect of temperature on the constant L.

The relative contents of trivalent iron in slag $M_{Fe_2O_3}$ also changes upon the introduction of CaO and SiO_2. However, the regularity observed here differs from that which took place in the case of slag-gas equilibrium /150/. As may be seen from fig. 225, the lines of equal $M_{Fe_2O_3}$ values now, i.e., upon contact with the metal phase, are no longer mutually parallel.

In the region of basic slags the angle of inclination of the curves towards the CaO—(FeO+Fe_2O_3) side of the triangle increases along with

the magnitude of $M_{Fe_2O_3}$. Moreover, the ratio $\frac{\alpha}{1-\alpha}$ turns out to be greater here than M'. Consequently, according to equation (VIII, 254), the concentration of O^{2-} ions (so long as α remains smaller than unity) drops along each line with the growth of CaO contents.

The results of these experiments, just as the data pertaining to the gas-slag equilibrium, apparently, speak in favor of the existence of anion $Fe_2O_5^{4-}$ and not of FeO_2^- ion. Indeed, if one should proceed from reaction (VIII, 227), then

$$K_4 = \frac{a^2_{FeO_2^-}}{a^3_{Fe^{2+}} \cdot a^1_{O^{2-}}}, \qquad \text{(VIII, 271)}$$

whence

$$M' = \frac{N_{FeO_2^-}}{N_{Fe^{2+}}} = K'_4 \cdot N'^{\frac{1}{3}}_{Fe^{2+}} \cdot N^{\frac{1}{3}}_{O^{2-}} \cdot \frac{\gamma'^{\frac{1}{3}}_{O^{2-}}}{\gamma_{FeO_2^-}}, \qquad \text{(VIII, 272)}$$

or, considering equation (VIII, 268)

$$M' = K''_4 \cdot \frac{N'^{\frac{1}{3}}_{Fe^{2+}}}{N'^{\frac{1}{4}}_{O^{2-}}} \cdot \frac{\gamma'^{\frac{1}{3}}_{O^{2-}}}{\gamma_{FeO_2^-}}. \qquad \text{(VIII, 273)}$$

From the obtained equation (VIII, 273) it does not follow sufficiently clearly that M' increases together with $N_{O^{2-}}$ when $N_{Fe^{2+}}$ = const. This would have been possible had the ratio $\gamma^{\frac{1}{3}}_{O^{2-}} / \gamma_{FeO_2^-}$ been increasing with growing concentration of Ca^{2+} ions faster than $N^{\frac{1}{4}}_{O^{2-}}$. However, the verity of precisely such rates of increment of the cited quantities calls for special proofs.

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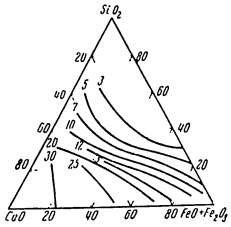

Fig. 225. Relative contents of ferric oxide $\left[\frac{Fe_2O_3 \cdot 100}{FeO + Fe_2O_3}\%\right]$ in the system $CaO-SiO_2-(FeO + Fe_2O_3)$ at equilibrium with iron at 1400-1450°C.

On the other hand, in making use of reaction (VIII, 264) and the corresponding equation (VIII, 265), we find

$$M' = \frac{N_{Fe_3O_5^{4-}}}{N_{Fe^{2+}}} = K_3 \frac{\gamma_{O^{2-}}^{5} \cdot \gamma_{Fe^{2+}}^{3}}{\gamma_{Fe_3O_5^{4-}}} \times \times N_{Fe^{2+}}^{2} \cdot N_{O^{2-}}^{5} = K_3 \frac{\gamma_{O^{2-}}^{2}}{\gamma_{Fe_3O_5^{4-}}} \cdot N_{O^{2-}}^{1} \cdot N_{Fe^{2+}}^{2}. \quad \text{(VIII, 274)}$$

It can be easily seen therefrom, that with the concentration of Fe^{2+} ions being constant, the increasing CaO contents causes both $N_{O^{2-}}$ and the activity coefficients ratio to augment, i.e., it leads to the growth of M' in full conformity with experimental evidence.

It proves to be somewhat more difficult to explain the constancy of M' along the line of its equal values, where the drop of FeO concentration leads, as mentioned above, to simultaneous decrease of $N_{O^{2-}}$ and $N_{Fe^{2+}}$. However, it is possible to assume that the corresponding increment of the $\gamma^2_{O^{2-}} / \gamma_{Fe_2O_5^{4-}}$ factor, which causes the increase of $N_{Ca^{2+}}$, may be offset by the drop of $N_{O^{2-}}$ and $N_{Fe^{2+}}$.

On the Transfer Kinetics from Slag to Metal.

Regrettably, no direct measurements pertaining to the kinetics of the passage by O^{2-} and Fe^{2+} ions of the slag-metal interface are available at the present time. Yet a number of indirect data indicate that this stage of the process constitutes one of those which limit the development of the process of carbon combustion.

Two circumstances are significant in this respect. In the first place this refers to a certain parallelism between the rate of carbon burnout and the magnitude of the specific area of the slag-metal interface; in the second place — to the absence of direct relationship between the activity of ferrous oxide in slag and the contents of oxygen in metal.

Influence of the Specific Area.

The intensity of the migration of O^{2-} and Fe^{2+} ions from slag to metal, like the velocity of any heterogeneous process, must be proportional to the area of the phase interface. It is a well known fact that interaction between metal and slag accelerates appreciably with increasing interphase surface.

This, as a matter of fact, constitutes the basis for various methods of rapid purification of metal from impurities by treatment with strongly dispersed slag.

A similar regularity was revealed also during tests on the "direct" influence of gases on metal. No doubt, there exists a thin layer of slag here, and the process of carbon combustion certainly includes the stage of oxygen transfer across the slag-metal boundary.

Thus, for example, Schwartzmann, Samarin, and Temkin [151], in studying surface decarbonization in large and small induction furnaces, found that the product of the reaction rate constant k multiplied by the mass of metal m, divided by its superficial area S, comprised 0.28 g/cm^2 min. with the alloy weighing 35 grams, 0.20 g/cm^2 min. with the weight amounting to 4.0 kg., and 0.08 g/cm^2 min. at the weight of 7.0 kg.

In other words, the said quantity diminishes only 4 times, whereas the mass of metal grows 200 times. The relative constancy of the quantity $\frac{km}{S}$ evidences the existence of a proportionality between the carbon burnout rate constant and the specific area.

Analogous results were also obtained by Rybakov [152]. While conducting tests in Tamman's and induction furnaces, he came to the conclusion that the decisive factor determining the rate of metal decarbonization by air is constituted by the magnitude of the specific area (fig. 226).

In this respect the high reactivity of the metal drops ejected into slag or the gaseous phase by the bubbles of CO is also interesting.

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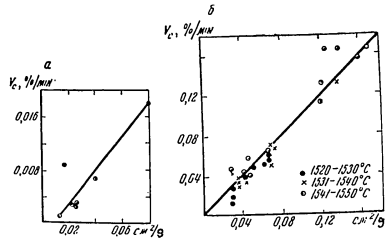

Fig. 226. Effect of the specific area of the metal mirror on the rate of carbon burn-out.

а – heat run in resistance furnace б – heat run in induction furnace

A direct study of this problem in industrial conditions, conducted by Medzhibozhsky, disclosed that the rate of carbon burn-out in all drops is 300-800 times greater than in the bath and is even 5 – 8 times greater than that in converters. The specific area of the drops increases thereby even more, namely 7500 times.

Of course, it does not follow absolutely from the cited date that only the passage by O^{2-} and Fe^{2+} ions of the slag-metal interface constitutes the slow stage of the process. They merely evidence that the processes determining the velocity must constitute some kind of heterogeneous transformations as well as the diffusion of substances towards the reaction surface. If at the same time, in conformity with the aforesaid, one should exclude oxygen transmission from gas to slag, then there will remain of the heterogeneous interactions only the passage of oxygen into metal and chemical desorption of carbon monoxide.

The absence of a strict proportionality between the rate of combustion and the specific area in the tests run by Schwartzmann, Samarin, Temkin, and Baptizmansky, and also a more rapid (4-6 times) progress of the process in induction furnace as compared with resistance furnaces (Rybakov's observations), point to the crucial significance of the hydrodynamic conditions. In all probability it is they that determine the convective diffusion of the reacting substances in the metal phase.

On the Relationship of Oxygen Concentrations in Metal and Slag.

The low rate of the transfer process across the metal-slag surface boundary constitutes essential evidence of the fact that the concentration of oxygen actually observed in steel turns out to be smaller than is required according to the conditions of metal equilibrium with slag

$$[O]_{fact} < [O]_{sl} . \qquad \text{(VIII, 275)}$$

This experimentally revealed inequality refers, evidently, to the mean contents of oxygen in metal. Yet, the conclusion pertaining to the absence of equilibrium is not refuted by the fact that the concentration of ferrous oxide is less near the surface of steel than in the bulk of slag. The fact of the matter is that in consequence of the reduction of trivalent iron anions the contents of O^{2-} and Fe^{2+} ions at this interface proves to be greater than in the entire remaining mass of slag. In view of this the inequality (VIII, 275) will only increase.

Furthermore, it is possible to assume that the actual concentration of oxygen in the metal layer bordering on slag is higher than the average. But the diffusion difficulties in the steel bath are hardly so great as to cause the oxygen concentration at the surface to correspond to that at equilibrium with slag which is strongly enriched by O^{2-} ions near the interface.

It is only natural then to infer that inequality (VIII, 275) is also observed at the interphase surface.

We shall dwell a little longer on the works confined to the problem of the relationship between the actual and equilibrium concentrations of oxygen in metal.

Schenk [61] departed from the fact that steel throughout the entire period of boil remains at equilibrium with slag as far as oxygen content is concerned. He believed erroneously that the rate of boundary penetration is much higher than the intensity of oxygen interaction with carbon.

He erroneously sought to explain from the positions of the molecular theory of slags the fact that the actual oxygen concentration in metal is lower than it should be according to the coefficient of equilibrium distribution. From his point of view, this indicated only that a certain proportion of ferrous oxide is to be found in a combined form in slag as silicate molecules.

A similar mistake was also made by Herasymenko [153], who maintained that the equilibrium of slag and metal with respect to oxygen is rapidly achieved, and does not limit the flow of the process. He incorrectly attributed the observed deviations from equilibrium distribution entirely to the influence of carbon on the activity coefficients of all metal components, i.e., in particular, also on γ_O.

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On the contrary, experiments show that oxygen content approaches that of equilibrium with slag only in such particular cases when the concentration of carbon is minor, i.e., when the consumption of oxygen per unit of time is small.

Investigations by a number of authors [154], [155], [156] lead to the conclusion that the reaction of oxygen with carbon in metal occurs more rapidly than the migration of O^{2-} and Fe^{2+} ions from slag to steel. By virtue of this fact the concentration of oxygen in the bath is appreciably lower than that at equilibrium with slag and is determined by the carbon contents.

Ageyev [157] also referred repeatedly to the slowness of oxygen migration from slag to metal.

Substantial support was given to these views by the works of Stark and Chelishchev [158], [159], [160]. During their studies in 1939-1941 of the results of heats run in basic open-hearth furnaces, they succeeded in establishing the fact that the contents of oxygen in steel does not grow with increasing velocity of carbon combustion.

For example, in high-speed heats (yield 11 t/m^2) the value of [O] not only failed to be higher, but was even lower than in ordinary runs (yield 4-6 t/m^2). These facts point to a slow-down in oxygen supply from slag to metal.

They also revealed that there is no parallelism whatsoever between the concentration of ferrous oxide in slag and the contents of oxygen in steel during the melting process. Thus, for instance, in a number of cases the latter quantity varied by 75-100% whereas the former remained practically constant.

Further, in the process of high-speed heats the concentration of FeO in slag dropped sharply without exerting any noticeable influence upon the magnitude of [O] fact.

A similar phenomenon was also observed during additions of ore — the value of (FeO) increased considerably without augmenting the oxygen contents in metal.

Thus, a detailed study of melting operations furnished the authors with ample grounds to refute the erroneous theory of equilibrium distribution of oxygen between steel and slag. In this connection they write that their investigations "have confirmed with sufficient definiteness Leiber's conclusion concerning the greater speed of the decarbonization process as compared with the speed of FeO transfer from slag to metal".

The foregoing, then, shows that the crossing of the slag-metal interface by O^{2-} and Fe^{2+} ions during decarbonization, like the migration of O^{2-} and S^{2-} ions during desulfurization, proceeds relatively slowly. According to the previously disclosed considerations, the speed of the stage under scrutiny is determinable, therefore, by a formula similar to the one introduced for the process of desulfurization, i.e.,

$$v = \frac{k_0 k_1 (O^{2-})(Fe^{2+}) - k_{-1} k_2 [O][Fe]}{[(O^{2-}) + k_2 [Fe]]^{a_1} [[O] + k_2 (Fe^{2+})]^{a_2}} . \qquad \text{(VIII, 276)}$$

Regrettably, in the absence of direct measurements of the intensity of FeO transfer it is impossible at the present time to compare the conclusions resulting from expression (VIII, 276) with actual experimental material. The time is amply ripe for corresponding investigations to be put in hand[1].

OXYGEN DIFFUSION IN SLAG.

Comparison of Diffusion and Reaction Rates at the Boundaries of Slag with Gas and Metal.

In passing over to the examination of diffusion processes in slag, let us first of all consider the motive force of diffusion. Let us leave aside for the time being the problem of intensive mixing caused by the bubbles of carbon monoxide.

From a comparison of the equilibrium diagrams (figs. 220 and 225) for reactions (VIII, 226) and (VIII, 227) it follows that the concentration of trivalent iron near the slag-gas interface is greater, and that of divalent iron smaller, than at the slag-metal interface. Moreover, the differences between $\Delta(Fe_2O_3)$ and $\Delta(FeO)$ increase with growing basicity of of slag.

It is also known that for homogeneous slags used in steel manufacture viscosity drops with the growth of basicity. The rise of the latter causes both an increase of the motive force and a reduction of the "resistance" to diffusion. In view of this, its rate augments.

Furthermore, if the rate constants of reactions (VIII, 226) and (VIII, 227) are comparable in magnitude with the diffusion coefficients of ferrous oxide and calcium ferrite, then the actually observed differences between the contents of Fe_2O_3 and FeO must diminish with increasing slag basicity. In an extreme case, if the rates of reactions (VIII, 226) and (VIII, 227) for some reason or other appear to grow in a degree equal to that of the growth of diffusion intensity, then the total gradients of Fe_2O_3 and FeO

1) According to the data produced by M. M. Karnaukhov, A. N. Morozov, and S. K. Chuchmaryov, the distribution rate of radioactive isotope Fe^{59} in steel bath is small in comparison with the exchange of Fe^{59} atoms between slag and metal. In order to arrive at a conclusive solution of the problem it is necessary, however, to study the kinetics of the transfer of other elements, for example, oxygen, sulfur, phosphorus, and so on.

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concentrations will remain unchanged.

In reality a different picture must be registered. The investigations conducted by Lapitsky and Medzhibozhsky for a number of heats run in different conditions show that the difference between Fe_2O_3 concentrations in the upper and lower layers of slag increase together with the ratio of CaO to SiO_2.

Fig. 227 illustrates the foregoing with regard to boiling metal. This bears witness to the fact that diffusion constitutes the limiting stage. It progresses much slower than reactions (VIII, 226) and (VIII, 227). Indeed, in spite of a certain acceleration caused by the decline of slag viscosity, diffusion appears to be incapable of levelling down noticeably the existing difference of concentrations.

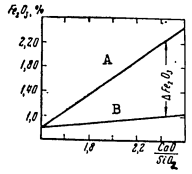

Fig. 227. Effect of slag basicity on the irregularity of ferrous oxide distribution along the height in slag.

A - Upper layer of slag; B - Lower layer of slag.

On the other hand, the reactions of oxidation (VIII, 226) and reduction (VIII, 227), developing at the boundaries of slag with gas and metal, proceed at such a rate that conditions arise which approach those of equilibrium. The flow of these reactions does not encumber the process as a whole. Reference to the first of them has been made above; as to the second, it belongs to the class of processes of charge-exchange of ions. As a rule, such processes proceed with great velocity.

It is essential to note that such a powerful additional factor as the mixing of slag by the evolving bubbles of carbon monoxide and the reguli of the sinking metal is also unable to equalize the concentrations of di- and trivalent iron. This fact only emphasizes the small value of the diffusion coefficients.

Speaking of the CO bubbles and the steel reguli, one should bear in mind not only their hydrodynamic effect upon slag, but also the chemical effect. According to a number of authors [82] up to 20% of the entire evolving carbon monoxide is used up in the reduction of iron oxides

$$FeO^{-}_{2\,(sl.)} + CO_{(gas)} = 2\,Fe^{2+}_{(sl.)} + 3\,O^{2-}_{(sl.)} + CO_{2\,(gas)}\,, \qquad \text{(VIII, 277)}$$

$$Fe^{2+}_{(sl.)} + O^{2-}_{(sl.)} + CO_{(gas)} = Fe_{(metal)} + CO_{2\,(gas)}\,. \qquad \text{(VIII, 278)}$$

In addition to this, the beads of steel which penetrate into slag are also major consumers of iron oxides. Actually, the intensive oxidation of these beads assures, according to Baptizmansky, the burn-out of up to 20% of the entire amount of carbon.

The foregoing makes it impossible to accept the distribution of concentrations that is often suggested in the literature [76], [161]. According to this outline, the contents of di- and trivalent iron are constant in the slag bulk and do not depend on the thickness of its layer. On the other hand, near the contact surfaces of slag with gas and metal the concentrations of FeO and Fe_2O_3 rapidly sink to zero (fig. 228).

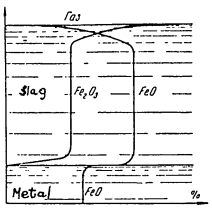

Fig. 228. Scarcely probable diagram of distribution of ferrous and ferric oxide concentrations along the height of the slag layer.

However, the assumptions that

$$N_{FeO.\,I} = 0; \quad N_{Fe_2O_3.\,II} = 0, \qquad \text{(VIII, 279)}$$

contradict the conditions of equilibrium. As mentioned previously, slag contains concentrations of ferrous and ferric iron comparable in magnitudes even at the surface of contact with air at a temperature of 1592°C.

The invariability of slag composition along the height also conflicts with direct measurements reported earlier. Such distribution throughout the slag mass is probably rarely achieved in furnace. It corresponds to very intensive stirring capable of eliminating completely the concentration

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differences within the slag.

Comparison of the Intensities of Diffusion and Slag-Metal Boundary Penetration.

Regrettably, no direct measurements have been made so far of the diffusion coefficients for ferrous oxide (i.e., for the simultaneously moving O^{2-} and Fe^{2+} ions) and calcium ferrite (i.e., Ca^{2+} and FeO_2^- ions)

An attempt was made by Ageyev [517], [627], [637] to evaluate the magnitude of the diffusion flow ($D_1 = D\frac{dc}{dx}$) for ferrous oxide in the system $FeO-SiO_2$. To achieve this, he employed the experimentally determined values of viscosity and surface tension. Calculations were made on the basis of Stokes' equation and the exponential temperature dependence of viscosity. At the same time the energy of activation was identified with the "surface" energy of formation of microcavity equal in size to the diffusing particle.

The values of D_1 which he determined were of the order of 10^{-6} g/cm^2 sec. over a temperature interval ranging from 1400 to 1470°C. Since the ions of FeO_2^- and Ca^{2+} are large in size, it is reasonable to expect that the D_1 value for calcium ferrite should be even smaller.

According to Ageyev's calculations, diffusion in these conditions can assure but a negligible rate of carbon burn-out equal to 0.00025% per hour, instead of the usual 0.2-0.4% (per 12 m^2 mirror area). This is in perfect agreement with the fact that noticeable gradients of di- and trivalent iron concentrations are to be registered in slag even upon intensive mixing caused by the CO bubbles.

In passing over to the comparison of the intensities of diffusion and penetration by the O^{2-} and Fe^{2+} ions of the slag-metal interface, let us make the following remark.

The diffusion of ferrous oxide constitutes a stage parallel to the crossing of the surface boundary. The available O^{2-} and Fe^{2+} ions either pass into metal or move away from it towards the gaseous phase. In other words, the mentioned ions participate simultaneously in two parallel processes.

On the other hand, the stage of calcium ferrite diffusion is successively followed by the passage across the slag-metal boundary. Actually, the FeO_2^- anions on reaching the surface are rapidly reduced to Fe^{2+} and O^{2-} ions whereupon the latter migrate into steel.

To evaluate the specific rate of this transfer Ageyev used equation

$$v = 3{,}1 \cdot 10^3 \sqrt{T} \cdot n \cdot e^{-W/kT}, \qquad \text{(VIII, 280)}$$

where n is the number of FeO particles per 1 cm^3;
W is the activation energy of the process;
k is Boltzmann constant.

Assuming that NW = 16.5; kTN = 57750 cal; n = $1.50 \cdot 10^{21}$ (20% FeO) and T = 1850 K, he found that v = $1.7\ 10^{-3}$ g/cm^2 sec. The produced values fully correspond to the acdeptable rates of decarbonization (0.48% C per hour per 12m^2).

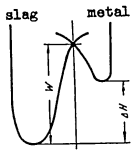

Fig. 229. Diagram of the location of the potential "holes" in slag and metal.

As Ageyev reasonably points out, the magnitude of the energy of activation is most essential in this evaluation. It was stated earlier that the heat of solution of liquid FeO in iron is great in absolute value and amounts to ΔH = 27,450 cal. This indicates that there are considerable energy obstacles to the passage by O^{2-} and Fe^{2+} ions of the slag-metal boundary.

To the extent that the process is accompanied by heat absorption, the potential "hole" in slag must be deeper than in metal (fig. 229).

In other words, one should expect that

$$W > \Delta H.$$

In view of this, the possibility is not excluded for the activation energy to have values not too remote from that adopted above - 58,000 cal. At any rate, its value should range somewhere within the limits of 27,450 and 58,000 cal.

Be that as it may, the recorded data indicate that the rate of slag-metal boundary crossing is approximately 10 times greater than the intensity of normal molecular diffusion in slag. The progress of a steady process of carbon combustion requires an equality of the successive stages. Such equalization occurs apparently as a result of diffusion acceleration by intensive stirring, and also in consequence of sporadic introduction of ore lumps which come into direct contact with metal.

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EQUILIBRIUM OF THE REACTION OF CARBON BURN-OUT.

Supposing a metal melt composed of Fe, C, and O is in contact with a mixture of CO and CO_2 gases. This ternary (Fe, C, O) biphase system possesses three degrees of freedom

$$f = k + 2 - n = 3 + 2 - 2 = 3. \qquad \text{(VIII, 281)}$$

In other words, out of the seven variables (P, T, p_{CO}, p_{CO_2}, N_{Fe}, N_C and N_O) which characterize the system's state, only three are independent. Indeed, in the state of equilibrium the cited variables are related by four equations:

$$P = p_{CO} + p_{CO_2}, \qquad \text{(VIII, 282)}$$

$$N_{Fe} + N_C + N_O = 1, \qquad \text{(VIII, 283)}$$

$$K_1 = \frac{p_{CO_2}}{p_{CO} \cdot a_O} = \varphi_1(T), \qquad \text{(VIII, 284)}$$

$$K_2 = \frac{p_{CO}^2}{p_{CO_2} \cdot a_C} = \varphi_2(T). \qquad \text{(VIII, 285)}$$

Of these the two last constitute the expression for the equilibrium constants of reactions

$$CO_{(gas)} + O_{(met)} = CO_{2,\,(gas)}, \qquad \text{(VIII, 286)}$$

$$CO_{2,\,(gas)} + C_{(met)} = 2\,CO_{(gas)}. \qquad \text{(VIII, 287)}$$

Either of them can be replaced by the following equation, resulting from their summation

$$C_{(met)} + O_{(met)} = CO_{(gas)}. \qquad \text{(VIII, 288)}$$

The corresponding equilibrium constant has the following aspect

$$K_3 = \frac{p_{CO}}{a_C \cdot a_O} = \varphi_3(T). \qquad \text{(VIII, 289)}$$

It follows from this equation that, at given carbon monoxide pressure, the product of carbon and oxygen activities (m) is determinable only by temperature

$$m = \frac{p_{CO}}{K_3} = a_C \cdot a_O = \varphi(T). \qquad \text{(VIII, 290)}$$

To make this system of equations applicable to the solution of concrete numerical problems, it is necessary to find the temperature dependence of m and K_2 (or m and K_1) as well as the relationships between the activities and the concentrations of carbon and oxygen.

Effect of Temperature. (Reaction $\underline{C} + \underline{O} = CO$)

It should be noted that highly under-rated values of m were produced in a number of relatively early laboratory studies. Thus, according to one set of data it comprised 0.00011 at 1550°C [164]; according to other data it varied from 0.00036 [165] to 0.0032 [166] (for a fairly detailed review of early works see [167], [168]). Only during the last two decades has it become possible to achieve a sufficiently well coordinated and more or less reliable evaluation of the values of m or K_3.

Thus, in one of the works [169] equilibrium was studied at 1620°C for minor concentrations of carbon (from 0.01 to 0.94% C).

It was determined thereby that

$$[C]\,[FeO] = 0{,}011, \qquad \text{(VIII, 291)}$$

or

$$[C]\,[O] = 0{,}00245. \qquad \text{(VIII, 292)}$$

This value was later confirmed in a more accurate investigation [170] carried out at 1580°C. Similar results were obtained [171] for carbon contents not exceeding 0.1%. It was revealed that at 1520°C

$$[C]\,[O] = 0{,}0020, \qquad \text{(VIII, 293)}$$

while at 1720°C

$$m = 0{,}0025. \qquad \text{(VIII, 294)}$$

Almost all the quantities cited are in satisfactory accord with the old calculations made by Le Chatelier [172] on the basis of solubility data for carbon (5.5%) and oxygen (0.24%).

As to the form of temperature dependence, this was established in one of the studies [167] on the basis of indirect data. Direct method was used for the study of the equilibrium of reaction

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$$FeO_{(melt)} + H_{2.\,(gas)} = Fe_{(melt)} + H_2O_{(gas)}, \qquad \text{(VIII, 295)}$$

for which it was determined that

$$\lg \frac{p_{H_2O}}{p_{H_2}\,[\%\,FeO]} = \frac{10\,200}{T} - 5{,}50. \qquad \text{(VIII, 296)}$$

Then, by utilizing the data for reactions

$$C_{(melt)} + CO_{2.\,gas)} = 2\,CO_{(gas)};\ \Delta F^\circ = 41\,980 - 34{,}45\,T. \qquad \text{(VIII, 297)}$$

$$H_{2\,(gas)} + \frac{1}{2}\,O_{2.\,gas)} = H_2O_{(gas)};$$

$$\Delta F^\circ = -60\,200 + 13{,}97\,T, \qquad \text{(VIII, 298)}$$

$$CO_{(gas)} + \frac{1}{2}\,O_{2.\,gas)} = CO_{2.\,(gas)};$$

$$\Delta F^\circ = -66\,500 + 20{,}16\,T, \qquad \text{(VIII, 299)}$$

it was established that

$$\lg \frac{p_{CO}}{[\%\,C]\,[\%\,FeO]} = \frac{2400}{T} + 0{,}675, \qquad \text{(VIII, 300)}$$

whence, at p_{CO} = 1 atm

$$\lg m = \lg [\%\,C]\,[\%\,O] = -\frac{2400}{T} - 1{,}327. \qquad \text{(VIII, 301)}$$

Relatively close results were also obtained in consequence of a direct investigation into reaction (VIII, 288).

The experiments /1687 were carried out in a hermetically sealed induction furnace, over a temperature range of 1500-1700°C at different CO pressures, with alloys containing up to 2.5% C. For p_{CO} = 1 atm, and /%C/ < 0.02, the results produced may be encompassed by equation

$$\lg K_3' = \lg \frac{p_{CO}}{[\%\,C]\,[\%\,O]} = \frac{1860}{T} + 1{,}643. \qquad \text{(VIII, 302)}$$

It is evident that expression (VIII, 302) differs but slightly from equation (VIII, 300).

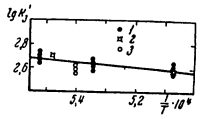

Fig. 230. Effect of temperature upon log K_3' as per data of different authors.

1 - /1687; 2 - /1717; 3 - /1707.

The data originating from tests /1687 are represented in fig. 230 where different symbols designate the values of log K_3 produced by other authors.

THERMAL EFFECT

From formulas (VIII, 301) and (VIII, 302), as well as from equations (VIII, 293) and (VIII, 294), it follows that the magnitude of m grows together with temperature. This indicates that reaction (VIII, 288) is exothermic. Yet, its thermal effect ΔH_3, according to equation (VIII, 302), is small and amounts to only 8500 cal/mole.

It should be noted here that up to the present time the question concerning the sign of the thermal effect of reaction (VIII, 288) still remains debatable. In the early works calculations were made without any allowance for the heats of carbon and FeO solution in metal. The inadequacy of such an approach was emphasized, for instance, in the studies by Baykov /1737 and other authors /1747. It is to be regretted that erroneous methods of thermal effect evaluation still continue to be used today. Thus, in the opinion of Yatsunskaya "carbon oxidation by ferrous oxide in metal" proceeds with the liberation of 31600 cal/g-atom C /1757.

Further, Gluskin, in his experimental studies of the temperature effect on the equilibrium of the Fe-O-C system, obtained values for m close to those cited above. However, he established that the equilibrium constant of reaction (VIII, 288) does not diminish, but on the contrary grows with temperature. Thus, for 1560°C he reports K_3 = 399.9, and for 1680 C - K_3 = 622.4.

Hence the product /%C/·/%O/ would amount to 0.0024 at 1560 and 0.00147 at 1680°C. On the basis of these data, Gluskin develops equation

$$\lg \frac{p_{CO}}{[\%\,C]\,[\%\,O]} = -\frac{5570}{T} + 2{,}7, \qquad \text{(VIII, 303)}$$

from which it transpires that ΔH_3 = + 27000 cal/mole.

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This value of thermal effect is too high and cannot be reconciled with the available data pertaining to the heats of solution.

On the other hand, a critical analysis of the data concerning the reaction under scrutiny effected by Stark [176] led him to the conclusion that the exothermic character ($\Delta H < 0$) of the decarbonization process is hardly subject to any doubt.

According to Kostovtsev [137], who compared the data on elasticity of iron oxide dissociation with the results of investigations of equilibrium in the Fe-O-H system, the thermal effect ΔH_3 also proves to be small.

In his judgment, there still are no data accurate enough for the evaluation of the magnitude and the sign of ΔH_3 at the present time. It is true that attempts to calculate ΔH_3, with consideration of the heats of carbon and ferrous oxide solution, often lead to directly opposite results. Thus, for example, according to Trubin and Oyks [42] it turns out to be negative ($\Delta H_3 = -4920$ cal/mole), i.e., the reaction is exothermic, while in other studies [171] it appears to be positive ($\Delta H_3 = 4000$ cal/mole), i.e., the reaction is endothermic.

It therefore must be recognized that this problem necessitates further experimental study.

Reactions $\underline{C} + CO_2 = 2\,CO$ and $\underline{O} + CO = CO_2$

Measurements of equilibrium compositions for metal with a low content of carbon reveal [168] that for reaction (VIII, 287)

$$C_{(met)} + CO_{2\ (gas)} = 2\,CO_{(gas)}$$

there exists a linear relationship between $\log K_2$ and $\frac{1}{T}$ in the first approximation (fig. 231). It can be represented by equation

$$\lg K_2 = \lg \frac{p^2_{CO}}{p_{CO_2} \cdot a_C} = -\frac{5778}{T} + 5{,}784\,, \qquad \text{(VIII, 304)}$$

whence

$$\Delta F^\circ_2 = 26\,400 - 26{,}45\,T. \qquad \text{(VIII, 305)}$$

From the above expression, it follows that the process is strongly endothermic ($\Delta H_2 = 26{,}400$ cal).

Fig. 231 shows points plotted according to the data of other authors. They appear to be either above [171] or below [170] the traced straight line.

A comparison of equation (VIII, 305) with the previously recorded formula (VIII, 297) emphasizes their strong divergence, in particular, with respect to the magnitude of the thermal effect. Yet, the values of ΔF°_2 calculated on the basis of both formulas do not differ very much, as may be seen from the following tabulation

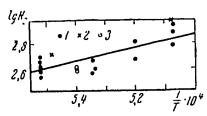

Fig. 231. Temperature dependence of the equilibrium constant K_2 according to the data of different authors:
1 - [168]; 2 - [171]; 3 - [170].

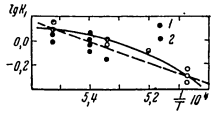

Fig. 232. Temperature effect on the equilibrium constant K_1, as per:
1 - [168]; 2 - [170].

$T°$, K	1800	2000	2200
ΔF_2 (VIII, 297)	— 20 030	—26 920	—33 810
ΔF_2 (VIII, 305)	— 21 210	—26 500	—31 790

The temperature dependence of the equilibrium constant for reaction (VIII, 286)

$$CO_{(gas)} + O_{(met)} = CO_{2\ (gas)}$$

may be expressed by equation

$$\lg K_1 = \frac{p_{CO_2}}{p_{CO} \cdot a_O}\,, = \frac{7320}{T} - 4.52. \qquad \text{VIII, 306)}$$

which corresponds to the dotted straight line in fig. 232 which passes near the experimental points [168].

However, the thermal effect resulting from this equation is in poor agreement with other published data, which fact serves as an indication of the insufficient accuracy of measurements [168]. Somewhat better are the results when $\log K_1$ is determined by indirect method from equation (VIII, 296) and the equilibrium constant of water gas reaction. In this case the temperature dependence assumes the aspect of

$$\lg K_1 = \frac{7320}{T} - 3{,}96\,. \qquad \text{(VIII, 307)}$$

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EFFECT OF CARBON CONCENTRATION (EXPERIMENTAL DATA)

The relationships recorded above were obtained from the data resulting from tests with low-carbon alloys. In such very dilute solutions the activities of carbon and oxygen practically coincide with the respective concentrations.

However, the absolutely obvious non-equivalency of the atoms of Fe, C, and O makes it possible to presuppose that they cannot form ideal solutions. Hence, the increase of carbon contents must lead to deviation of γ_C and γ_O coefficients from unite and, consequently, require a definition of their dependence upon composition.

In this respect it is interesting to study, for instance, the effect produced by the concentration of C upon the quantity m' which according to equation (VIII, 290) is inversely proportional to the product $\gamma_C \cdot \gamma_O$.

$$m' = [C][O] \frac{m}{\gamma_C \gamma_O}. \qquad \text{(VIII, 308)}$$

In conjunction with the aforesaid, the product of carbon and oxygen concentrations (m') will be almost constant in poor alloys and variable in rich ones.

Individual observations have indicated for quite some time now that m' grows with [%O]. For example, at 0.1% C the value of m' turned to be equal to 0.0025, while at 2% C it reached 0.01. However, it should be borne in mind that these results were obtained on the basis of analyses of steel from open-hearth baths. Its composition ordinarily deviates more from equilibrium, the greater the percentage of carbon. It follows therefore that the activity coefficients γ_O and γ_C cannot be judged on the basis of these data.

More reliable are the laboratory experiments conducted at different CO pressures (from 1 to 20 atm) and carbon contents ranging from 0.1 to 2% C [168].

The results of these measurements refer to the temperature of 1540°C and are recorded in fig. 233. They show that the product m' grows more along with [%C] the higher the pressure of CO. Thus in accordance with these experiments, the activity coefficients of carbon and oxygen change together with the alloy composition.

For the determination of the dependence of γ_C on the percentage of carbon, use was made of the fact that p^2_{CO}/p_{CO_2} is in direct proportion to the concentration of C, when its contents do not exceed 5%. This means that within the mentioned limits expression

$$K_1 = \frac{p^2_{CO}}{p_{CO_2}[\%\ C]}$$

constitutes the equilibrium constant. According to experimental data, its value amounts to 430 at 1540°C.

Moreover, it can be seen from equation (VIII, 285) that, according to the above fact, $\gamma_C = 1$ within the limits of the mentioned concentrations. At different carbon concentrations, the value of γ_C may be determined from equation

$$\gamma_C = \frac{p^2_{CO}}{p_{CO_2}[\%\ C] \cdot 430}. \qquad \text{(VIII, 309)}$$

The values of the activity coefficients γ_C, calculated from equation (VIII, 309), are compared in table 36 with the data obtained by other methods by authors [47], [177], [178]. From table 36 it transpires that the values of γ_C determined by different independent methods prove to be the higher, the greater the concentration of C.

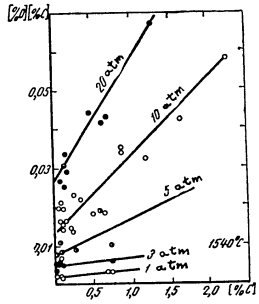

Fig. 233. Dependence of [%C]·[%O] on the pressure of carbon monoxide and the composition of carbon in iron at 1540°C.

As to the activity coefficient of oxygen, it was determined on the basis of the fact that the activity of oxygen in carbon-free metal coincides with its percentage for all concentrations up to saturation. Consequently, for small carbon concentrations, where $\gamma_C = 1$ and $\gamma_O = 1$, the value of the equilibrium constant

$$K_1 = \frac{p_{CO_2}}{p_{CO}[\%\ O]\,\gamma_O}$$

may be computed directly from the equilibrium composition of phases. Extrapolation with respect to [%C] = 0 gives $K_1 = 1.21$ at 1540°C. Hence,

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$$\gamma_O = \frac{p_{CO_2}}{p_{CO}\,[\%\ O]\ 1{,}21}. \qquad \text{(VIII, 310)}$$

Table 36

Dependence of the activity coefficient of carbon upon its concentration according to the data of different authors.

[%C]	γ_C as per data of		
	[168]	[177]	[178] and [4]
0,1	1,00	1,02	1,00
0,2	1,00	1,04	1,04
0,5	1,00	1,12	1,11
0,75	1,01	1,19	—
1,0	1,03	1,27	1,23
1,5	1,08	1,46	1,46
2,0	1,23	1,73	1,65

Samarin, Polyakov, and Schwartzmann [179] elaborate the same experimental data in a somewhat different manner.

In discussing the causes for the influence of carbon concentration on the magnitude of m', they assume its deviation from constancy to be related to the behavior of oxygen, i.e.,

$$m = [\%\ C]\,[\%\ O]\,\gamma'_O. \qquad \text{(VIII, 311)}$$

Inferring, further, that for [%C] $\leqslant$ 0.01 and 1540°C, $\gamma_O = 1$, they find that m $\simeq$ 0.0018, whereupon

$$\gamma'_O = \frac{0{,}0018}{[\%\ C]\,[\%\ O]}. \qquad \text{(VIII, 312)}$$

It is evident that the values of γ', calculated in this manner, will not differ at all from the product ${}^{0}\gamma_O \cdot \gamma_C$.

Table 37 lists the values of the activity coefficients of oxygen computed from equations (VIII, 310) and (VIII, 312).

A comparison of the data from tables 36 and 37 reveals that the coefficient γ_C grows, while the value of γ_O and the product $\gamma_C \cdot \gamma_O$ drop with increasing carbon concentration.

Table 37

Activity coefficients of oxygen depending on the contents of carbon.

[%C]	γ_O as per Yessin's data	$\gamma_O \cdot \gamma_C$	γ_O as per data [71]
0,0	1,00	1,00	1,00
0,1	0,93	0,93	0,89
0,2	0,86	0,86	—
0,3	0,79	0,79	—
0,5	0,67	0,67	0,69
1,0	0,50	0,515	0,515
1,5	0,42	0,454	—
2,0	0,39	0,48	0,345

DISCUSSION OF THE RESULTS OBTAINED

In explaining the causes for the deviation of the activity from concentration, certain authors [168] unjustifiably assume the existence in liquid metal (along with the atoms of C, Fe, and O) of molecules of CO, FeO, and Fe_3C. As reported in Chapter VII, such inferences are not consonant with facts (see also [180]).

With doubtful consistency these authors, while acknowledging the presence in the melt of a number of molecules (Fe_3C, FeO, CO), then center their attention only on one type, namely the CO particles. It should be noted that a similar erroneous conclusion (existence of CO molecules in liquid Fe) has also been made before [181].

By substituting in the expression of equilibrium constant the quantity ([%C] - 0.0012 p_{CO}) for the activity of carbon and ([%O] - 0.0016p_{CO}) for the activity of oxygen, they obtain

$$K'_3 = \frac{p_{CO}}{([\%\ C] - 0{,}0012\,p_{CO})\,([\%\ O] - 0{,}0016\,p_{CO})} \qquad \text{(VIII, 313)}$$

and strive to secure a constant value for K'_3. In other words, this method permits the reconciling of the experimental data with the ideal law of mass action.

It was stated previously, however, that the dissolution of a number of diatomic gases in metals is accompanied by the destruction of their molecules. As a matter of fact, during solution of carbon monoxide in iron a decomposition reaction takes place which breaks the CO molecules up into C and O atoms.

This study [168] was thoroughly analyzed by Stark [176]. Quite justifiably, he rejects as totally groundless the postulate concerning the existence in metal of CO molecules. At the same time, Stark believes that the conclusion pertaining to the variability of the activity coefficients is also wrong. He thinks that it came as a result of the fact

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that no equilibrium could be achieved in these experiments at concentrations [%C] ≥ 1%.

This deduction cannot be accepted though. The fact of the matter is that the growth of coefficient γ_C with the contents of carbon was also revealed by other authors [177] and by means of other methods [47] (see also part I of the present monograph).

In investigating industrial heats, Chuyko was able to establish that for reactions (VIII, 288) and (VIII, 288'), i.e.,

$$C_{(met)} + O_{(met)} = CO_{(gas)},$$
$$C_{(met)} + FeO_{(sl)} = CO_{(gas)} + Fe_{(met)}$$

the pressures of CO are different and they are greater for the second than for the first

$$p''_{CO} > p'_{CO}.$$

Only one fact transpires thereby that the system was not in a state of equilibrium. Yet he draws a conclusion to the effect that the activity coefficient of oxygen is independent of the concentration of carbon.

No more conclusive is his statement that from the totally unsubstantiated relationship

$$[\% C] = [\Sigma C] \cdot \gamma_C \qquad \text{(VIII, 314)}$$

it follows allegedly that the coefficient γ_C drops with the increase of total carbon concentration [ΣC].

Little is conveyed by Baptizmansky's efforts to prove the constancy of γ_C and γ_O on the basis of kinetic data (on the weak dependence of the rate of carbon burnout upon its contents in metal).

In a series of works by Samarin and co-authors, an attempt is made to explain the variability of coefficients γ_C and γ_O without resort to the hypothesis concerning the existence in molten metal of molecules of CO, Fe_3C, and so on. The point of departure here is constituted by the postulates developed by Temkin and Schwartzmann. According to the latter, the deviations from ideal solutions, observed in iron alloys, are caused mainly by spatial limitations in the arrangement of the atoms of the solute.

How the growth of coefficient γ_O with the concentration of carbon is explained from this point of view was described earlier.

In discussing the variation of coefficient γ_O Samarin and Schwartzmann [182] observe that "oxygen, unlike carbon, does not dissolve in iron according to the intrusion pattern, and its solubility can therefore be

considered as directly proportional to the magnitude of the free volume in liquid iron."

With the increase of the latter (equal to the difference between the volumes of liquid metal V and solid metal W) the spatial limitations diminish and the activity coefficient of oxygen augments. Moreover, it is assumed that γ_O changes simply in inverse proportion to the free volume

$$\gamma_O = \frac{b}{V - W}. \qquad \text{(VIII, 315)}$$

In other words, relationship (VIII, 315) is substantiated only qualitatively and not quantitatively.

At melting point the specific volume of solid iron W = 0.1361, that of liquid iron at 1600°C - V = 0.1397. Assuming that in the latter case $\gamma_O = 1$, we find b = 0.0036, whence

$$\gamma_O = \frac{0,0036}{V - 0,1361}. \qquad \text{(VIII, 316)}$$

From equation (VIII, 316) it follows that carbon concentration may exert an influence on coefficient γ_O only as a result of a change in the specific volume of liquid iron V. The latter increases with growing carbon contents which leads to diminishing γ_O.

Table 38 provides a comparison of the γ_O values calculated from formula (VIII, 316) with those determined experimentally. As may be gathered from this comparison, equation (VIII, 316) reflects correctly only the general tendency of γ_O to diminish with increasing carbon percentage. No quantitative accord with the experimental data is to be registered.

Table 38

Comparison of observed and calculated values of γ_O.

[%C]	γ_O	
	as per experimental data	as per formula (VIII, 316)
0,0	1,00	1,00
0,2	0,86	0,53
0,3	0,79	0,48
0,5	0,67	0,43
1,0	0,50	0,36
1,5	0,42	0,33
2,0	0,39	0,29

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This apparently should be attributed to the fact that equation (VIII, 316) reflects only one aspect of the influence of carbon, namely the increase of free volume. Indeed, in full accord with Bachinsky's ideas the viscosity of carbon-iron alloys sinks with the growth of carbon concentration (fig. 234).

However, apart from this, the introduction of carbon changes the interaction energy of the melt atoms, particularly those of oxygen. In this connection it is well to mention the experiments of Gruzin, Kornev, and Kurdyumov [184] who, by means of radioactive iron isotope Fe^{59}, studied the coefficient of self-diffusion in γ_{Fe}. It appeared (fig. 235) that it diminishes with increasing carbon percentage, although the energy Q of the lattice loosening decreases too.

Formula

$$D = 10^{-[\%C]} \exp\left\{-\frac{69000 - 7000\,[\%\ C]}{RT}\right\} \qquad \text{(VIII, 317)}$$

evidences that the mobility of iron atoms declines with growing concentration of carbon atoms, while the "free" volume of the system augments (in consequence of dropping Q).

In summing up the foregoing, it is necessary to underscore the fact that experimentally the problem has been insufficiently studied. This, to a considerable degree, is due to the difficulties involved in achieving true equilibrium in correct sampling and reliable determination of the oxygen concentration.

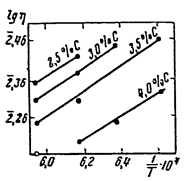

Fig. 234. Effect of temperature and carbon contents on the viscosity of cast-iron.

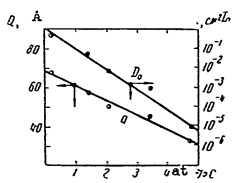

Fig. 235. Dependence of the coefficient Q and D_0 from equation $D = D_0 \exp\left\{-\frac{Q}{RT}\right\}$ on carbon contin austenite.

A -- Kcal/g-atom; B -- D_0 cm^2/sec.

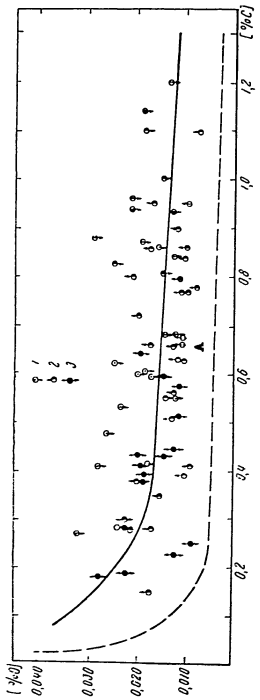

Fig. 236. Relationship between [% O] and [% O] in metal according to the data of industrial tests:

1 - samples in which the tendency towards [% O] decline was registered;
2 - same, with tendency of [% O] to increase;
3 - with undetermined direction of [% O] change.

A -- equilibrium curve.

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In spite of the insufficient precision of the relationships, the experimental materials still permit speaking of the variability of activity coefficients γ_C and γ_O. Moreover, one of them indubitably grows with carbon concentration, whereas the other apparently drops.

ACTUAL CARBON AND OXYGEN CONCENTRATIONS IN METAL BATH

The question of the actual carbon and oxygen contents in the bath of open-hearth furnaces is of substantial importance. Even on the basis of average data pertaining to the variation of their contents in the process of melting, it appears to be possible to make qualitative conclusions as to the inter-relationships between the rate constants of the individual stages of the process.

In their work [160] Stark and Chelishchev processed the data of 21 industrial heats in one and the same furnace. Samples of metal were taken during the run which allowed not only the determination of the contents of carbon and oxygen, but also the establishment of the tendencies in their variations (rise or drop).

The results of their investigation are represented in fig. 236 in the form of a solid curve above which are located points (1) corresponding to the sinking tendencies of the oxygen concentration, and below (2) those showing its tendency to rise. Thus, the recorded curve reflects the relationship between the contents of C and O in steel for a stabilized process of decarbonization. It is situated above the dotted curve which corresponds to equilibrium conditions [169].

The comparison consequently shows that the actual contents of oxygen in the bath is greater than at equilibrium

$$[O]_{fact} \quad [O]_{equil.}$$

Similar results were also produced by Stark and Filipov [185] in a small (8 kg) induction furnace. It became evident thereby that in runs under slag peroxidation is somewhat less than when the metal is "bare" in which case, incidentally, the percentage of oxygen fluctuates powerfully.

The same conclusions were reached by Samarin, Polyakov, and Schwartzmann [179], who analyzed the data observed by a number of investigators. As may be seen from fig. 237, the actual oxygen concentrations in metal (region B) are higher than those at equilibrium with carbon (curve A) and lower than those at equilibrium with slag (according to different data either region C, or region Д). Analogous conclusions were also made by other authors [186].

The data recorded here and numerous other observations indicate that some one of the stages develops in the metal bath relatively slowly and limits the process as a whole.

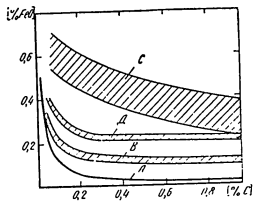

Fig. 237. Relationship between [% Fe] and [% C] in metal in the conditions of:

A -- equilibrium of [O] with [C]; B -- industrial heats; C and Д - equilibrium of metal with slag.

A form of relationship between the concentrations of C and O, other than (VIII, 308) considered above, may serve as an additional confirmation of the fact that the equilibrium of reaction

$$C_{(met} + O_{(met)} = CO_{(gas.}$$

fails to stabilize.

An illustration of the foregoing is provided in fig. 238 plotted by Oyks, Maksimov, and Kaluzhsky. It displays curves reflecting the variation of the equilibrium (a) and actual (δ) values of $m' = \frac{[\%O]}{[\%O]}$ with growing carbon contents. Fig. 238 shows that the actual value of m' is greater than that of the state of equilibrium and that this inequation increases with rising carbon concentration.

Analytic expressions were proposed for curve (δ). According to one group of investigators [186] its equation has the following aspect

$$[C]_{fact}\ [FeO]_{fact} = 0{,}0124 + 0{,}050[\%\ C]_{fact}\ . \qquad \text{(VIII, 318)}$$

A linear relationship similar to the above is advanced by other authors [187], [188]

$$[C]_{fact}\ [FeO]_{fact} = 0{,}012 + 0{,}087[\%\ C]_{fact}\ , \qquad \text{(VIII, 319)}$$

$$[C]_{fact}\ [FeO]_{fact} = 0{,}0146 + 0{,}032[\%\ C]_{fact}. \qquad \text{(VIII, 320)}$$

All these equations re-emphasize the fact that boiling metal is peroxidized, i.e., that it contains more oxygen than follows from the conditions of equilibrium.

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Which one of the transformations developing in the metal bath then proceeds insufficiently rapidly? Is it constituted by the chemical reaction between carbon and oxygen? Apparently not.

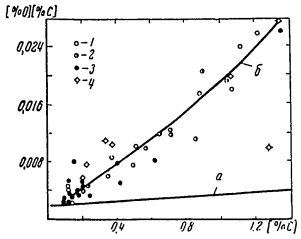

Fig. 238. Dependence of the product [% O] [% O] upon [% C] in equilibrium conditions (a) and in conditions of industrial heats (б) according to the experimental data of:

1 -- Oyks and co-authors; 2 -- Stark and Chelishchev; 3 -- Oyks; 4 -- Ageyev.

Indeed, the rate of the process of carbon burn-out increased hundreds of times when other methods were used assuring more intensive oxygen supply into the metal bath (bessemerizing, blowing of metal with oxygen or air in open-hearth or electric furnaces).

Consequently had the chemical reaction been the limiting stage, then it would have been reasonable to expect a far greater peroxidation of metal to take place, i.e., a very sharp divergence of the curves reflecting the actual and the equilibrium values of m'.

Yet this is not so. This is evidenced, in particular, by the location of curves (a) and (б) in fig. 239, which refers to oxygen-blowing of metal [189]. In spite of the great quantity of oxygen absorbed by the bath, its assimilation proceeds rapidly enough. Peroxidation (the divergence of plots a and б) remains approximately the same as in the case of a normal open-hearth furnace run.

Actually, as may be seen from fig. 239, concentrations $[FeO]_{fact}$ before, after, and during oxygen-blowing do not differ one from another and correspond to the limit characteristic for active boil (curve a).

Many other similar data pertaining to the assimilation of oxygen are reported in the book by Yatsunskaya and Starovich [175].

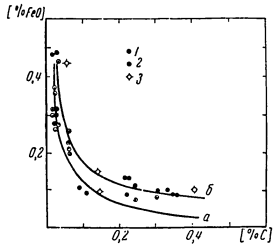

Fig. 239. Relationship between [% O] and [% C] in metal at equilibrium (a) and during blowing in converter (б):

1 -- samples taken prior to blowing; 2 -- same after blowing; 3 -- during blowing.

Analogous results were obtained by Maksimov [190] during a study of the Bessemer process. Here (fig. 240), as earlier, curve (2) of actual oxygen contents is to be found above curve (1) pertaining to equilibrium with carbon, and below curve (3) which refers to equilibrium with slag.

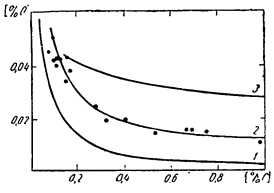

Fig. 240. [% O] versus [% C] in the conditions of equilibrium of dissolved carbon and oxygen (1), during Bessemer blowing (2), and at equilibrium of metal with slag (3).

Further, it appears that in the case under review the magnitude of m' grows with carbon contents slower than in the instance of open-hearth melting. The curves for $m'_{o\text{-}h.}$ and $m'_{Bes.}$ intersect when concentration [% C] = 0.3%. At greater carbon contents, open-hearth metal peroxidizes more than Bessemer metal; at lower carbon contents the process is reversed. According to Maksimov, this is due to the fact that the formation of CO bubbles is greatly impeded in the open-hearth furnace. This is not so in the Bessemer converter.

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The foregoing justifies the belief that the chemical reaction stage is not the limiting stage of the decarbonization process.

In summing up, it may be seen that the average actual contents of oxygen $[O]_{fact}$ may vary within the limits from equilibrium with carbon $[O]_C$ to equilibrium with slag $[O]_{sl}$. In cases conducive to the formation, growth, and elimination of carbon monoxide bubbles, the concentration $[O]_{fact}$ tends to approach $[O]_C$. Such is the case when the contents of carbon is small (up to 3%), when the quantity of the forming CO is not large, and there is a sufficient number of centers of generation for the formation of the bubbles.

In the case of metal blowing, the question of bubble formation does not arise and the question of supplying them with carbon becomes more important. Hence, the approximation of concentration $[O]_{fact}$ to $[O]_C$ becomes more explicit here with increased carbon concentrations.

It should be borne in mind that the equilibrium contents of oxygen $[O]_C$ corresponds to pressures exceeding 1 atm. As was repeatedly mentioned by Dobrokhotov, Andreyev, Karmazin, and other authors, the pressure of the melt layer and the forces of surface tension must be taken into account. In the opinion of a number of authors, total pressure in the bubble amounts to 1.5 - 3.0 atm.

In the converse case, when the formation of CO is strongly inhibited, the actual concentration of oxygen begins to grow and in a few special cases it may attain the magnitude of $[O]_{sl}$. Nevertheless, as a rule, it is smaller, i.e., the inequation $[O]_{fact} < [O]_{sl}$ continues to be observed. Most frequently this takes place when $[\%\ C] > 0.4\%$, i.e., when the quantity of oxygen consumed every second is sufficiently large.

In the opinion of Karmazin and Pukhnarevich [191], the elimination of carbon monoxide is strongly inhibited at the initial periods of melting, when not only the contents of carbon is relatively large, but the superheating of metal is insufficient, its viscosity is high, and the bassing surface small. In these circumstances peroxidation becomes so extensive that it leads to red-shortness of steel.

LOCATION OF THE REACTION FRONT

As mentioned earlier, the molecules of CO do not exist in liquid iron (see also [192]). Consequently, reaction (VIII, 288) $C_{met} + O_{met} = CO_{gas}$ is not homogeneous but heterogeneous. It develops at the boundary of metal with bubbles. In view of this, the reaction front is located where there are bubbles.

If these form at the furnace bottom and then make their way through metal into the furnace atmosphere, then reaction (VIII, 288) will take place at the hearth and within the volume of the entire bath. On the contrary, if the bubbles emerge only at the slag-metal interface, then the whole front of the reaction will concentrate there.

The possibility of bottom and surface ebulition was first substantiated by Andreyev [193] both by means of a study of the reaction of soda solutions with acetic acid (model), as well as by way of visual observations of boiling metal.

While conducting laboratory runs in an induction furnace with a thin layer of slag (10 mm), he noticed the formation of bubbles at the metal-slag interface. They are directly distinguishable by a light spot appearing at the surface of slag.

Apart from these relatively small bubbles, larger ones form near the bottom and penetrate through the layer of metal and slag.

Similar observations (with the aid of binoculars) were made by him also in the open-hearth furnace bath. Here too two types of bubbles evolve: large - bottom ones, and small - surface bubbles. The latter are to be registered after the charge of ore and they persist the longer, the lower the temperature of the bath. With consumption of ore and increasing temperature, the surface boil weakens and finally subsides altogether.

Depending on the conditions of the process (composition of slag and metal, their temperature, the presence and the nature of the non-metallic inclusions, the condition of the hearth and batters, etc.), different types of ebulition may therefore occur: - bottom boil only, surface boil only, or both together.

DISTRIBUTION OF THE CONCENTRATIONS OF ELEMENTS IN DEPTH IN THE BATH.

Data pertaining to the different locations of the reaction front may be obtained not only on the basis of visual observations of the frequency in the appearance of bubbles, their size and the energy of their rising, but also by means of a study of the distribution of concentrations of different elements (H, C, O, and so on) along the height of the bath.

The experimental difficulties here are sufficiently great, consisting not only in the requirement for simultaneous sampling of metal from different levels of the bath but also in that it is necessary to prevent subsequent interaction of the metal components in order to fix its initial composition.

Investigation into the distribution of carbon along the height of the bath of an open-hearth furnace shows that the degree of inhomogeneity

$$\alpha = \frac{N_{max} - N_{min}}{N_{aver}} \cdot 100\% \qquad \text{(VIII, 321)}$$

is small.

Thus, for instance, Chelishchev [194] succeeded in establishing the fact that the contents of carbon in samples taken simultaneously from three levels (500, 700, and 900 mm below the slag layer) differed only

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by 0.01- 0.02, and rarely by 0.05%, i.e., that it is almost the same. A similar constancy of concentration was also established for manganese.

These results are analogous to those published earlier by Karmazin [195], according to whom the contents of carbon and manganese during the hot run of furnace does not change in height, which fact points to intensive mixing in the bath caused by the evolving gases (table 39).

Table 39

Mn and C concentrations at the upper and lower levels of the bath

Near the slag		At the depth of 1300 - 1500 mm	
Mn	C	Mn	C
0,16	0,36	0,15	0,36
0,15	0,42	0,15	0,41
0,16	0,46	0,14	0,41
0,19	0,40	0,18	0,40
0,22	0,54	0,19	0,48
0,37	0,60	0,37	0,57

The minor dependence of carbon concentration on the height of the slag layer was also noted by other authors [196], [197].

In more recent works, it became possible however not only to confirm the small difference in carbon contents of Δ N in height, but also to expose the regularity of Δ N variation in the course of melting.

Thus, for instance, Oyks, Maksimov and Kaluzhsky [198], who studied the variation of concentrations of elements in the process of melting took samples simultaneously from three levels (100, 350, 600 mm. under the slag-metal interface). They succeeded in establishing that at relatively low temperatures carbon content in the upper layers is lower than at the bottom of the furnace. This difference levels down with heating and becomes inverse during the hot run of the furnace - carbon content in the lower sections of the bath turns out to be inferior to that in the upper layers.

A far greater difference in concentration along the cross-section of the metal layer is to be observed with regard to oxygen [199], [200], [198], [201], [154]. According to Yavoysky [202], the degree of irregularity in oxygen distribution is many times that of carbon and depends on the period of melting. It reaches a maximum at the end of ebulition with ore and at the beginning of the clear boil. Irregularity is greater during this period in 350-ton furnaces than in those with a capacity of 100 and 185 tons. Towards the end of clear boiling it drops to α = 40-50% and becomes closer for different capacity furnaces.

Fig. 241 illustrates the change in the character of oxygen distribution in depth during the transition from one melting period to another. It turns out that maximum oxygen concentration is to be registered in

different places - near the slag, or close to the bottom, or , finally, in the intermediate levels. This can be seen particularly clearly from fig. 242, where actual and equilibrium contents of oxygen are compared.

There is no doubt that such character of oxygen distribution, as well as that of carbon, is caused by the location of the reaction front.

Indeed, the presence of surface boiling is indicated by the fact that in a number of cases the difference Δ [O] between observed and equilibrium concentrations near the slag-metal interface is smaller than at the bottom and within the volume of the bath. This also is suggested by the fact that the least contents of carbon is to be registered in the layer situated immediately under slag. In brief, it transpires from these data that the reaction takes place in the proximity of the slag-metal interface. It is precisely here that the greatest drop in carbon and oxygen concentrations and their approximation to equilibrium values is to be observed.

In a converse case, when the contents of carbon and deviation of oxygen concentration from equilibrium prove to be minimum, the reaction front should be located close to or even at the bottom.

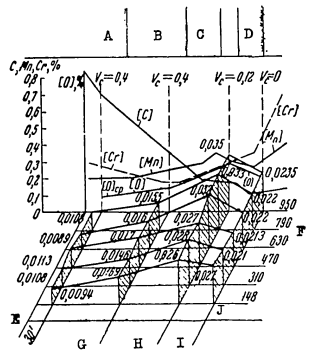

Fig. 241. Distribution of oxygen in depth of bath and change of its concentration in a heat run in 100-ton capacity furnace during chromium reduction process.
A -- Addition of ore and bauxite; B -- Additions of bauxite, lime and ferromanganese; C -- Tapping of slag; D -- Reduction and addition of ferrochromium; E -- Melting; F -- Distance from the bottom, mm; G -- 2 hrs 30'; H -- 4 hrs 20'; I -- 5 hrs 10'; J -- Bottom layer; K -- Time, hrs-min.

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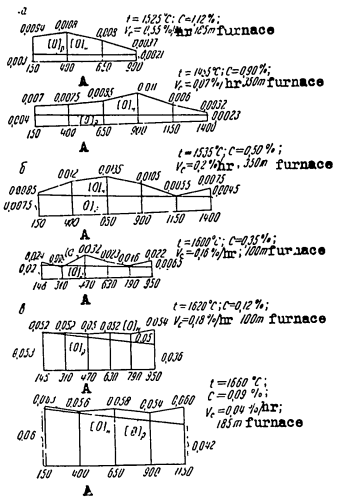
а
t = 1525°C; C = 1,12 %;
Vr = 0,35 %/hr; 185 m furnace
A
t = 1535°C; C = 0,90 %;
Vr = 0,07 %/hr; 350 m furnace
A
б
t = 1535°C; C = 0,50 %;
Vr = 0,2 %/hr; 350 m furnace
A
t = 1600°C; C = 0,35 %;
Vr = 0,16 %/hr; 100 m furnace
A
в
t = 1620°C; C = 0,12 %;
Vr = 0,18 %/hr 100 m furnace
A
t = 1660 °C;
C = 0,09 %;
Vr = 0,04 %/hr;
185 m furnace
A

Fig. 242. Oxygen concentrations - in equilibrium with carbon [O]p, and as observed in the bath [O]H:

а -- during sub-slag carbon oxidation; б -- during bottom volume oxidation of carbon; в -- during bottom boil of low-carbon metal.

A -- Distance from the bottom, mm.

Data pertaining to the distribution of hydrogen and nitrogen serve as an additional confirmation of the foregoing. Indeed it is reasonable to expect that during surface boil the bubbles of carbon monoxide will outgas the metal far less than during bottom ebulition when they are penetrating the entire volume of the bath.

As shown by Yavoysky's investigations [202], as well as those of other authors, the variations in N_2 and H_2 contents along the height of the bath are considerable and exceed those of oxygen concentrations. Depending on the melting conditions, three types of distribution are to be registered here. In one of them (A) the concentration of dissolved gas grows from the bottom to the surface of metal, in the second (B) it -- on the contrary -- decreases, while in the third case (C) - it changes irregularly along the height.

Type A distribution is characteristic for such periods of melting when the total oxygen contents in bath increases with time. Type B, on the contrary, corresponds to the conditions of general de-gasification of metal. It is probable that in the case of A there develops a surface boil which does not assure de-gassing and does not impede the passage of H_2 from the furnace gases through slag into metal. Hence, the gradient of concentrations peculiar to the process of H_2 and N_2 absorption by the bath is here preserved.

On the other hand, the B and C type distributions are characteristic for bottom ebulition during which the CO bubbles intensively[1] remove N_2 and H_2.

The fluctuation limits of the degree of distribution irregularity for different elements in furnaces with different capacities [201] are recorded in table 40.

Table 40

Degree of Distribution Irregularity of Elements

Furnace capacity, m.	Irregularity, %, for elements:						
	C	Mn	S	P	O	N	H
350	1—8	6—27	3—17	1—10	30—80	18—85	38—130
185	0—20	5—18	4—12	7—23	13—51	12—46	59—151
100	1—15	7—25	20—60	0—60	10—80	10—50	20—110

BOTTOM AND SURFACE BOILING

The recorded material confirms Andreyev's observations and indicates that there exists a possibility for the reaction front to be located either at the metal-slag interface (surface boil), or at the interface with the hearth bed (bottom boil) and at the surface of the emerging bubbles.

As proved by tests, the surface boil characterized by the formation of a great number of small bubbles, develops the more intensely the lower the temperature of metal. In this case the metal is cold, viscous, and insufficiently super-saturated in the bottom layers with respect to the reaction of burn-out.

Surface boil is also facilitated by increased carbon contents and greater oxidizing capacity of slag. It is enhanced by poor penetrability of slag, i.e., large quantity of solid particles close to the surface boundary.

Stark and Chelishchev [158], [159], [160] are even apt to accept the one-sided assumption that the reaction front concentrates mainly at

[1] The degassing character of the boil was proved by Yavoysky also by special tests on bath sparging by nitrogen, carbon dioxide and dry air [202].

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the boundary of liquid phases. In their judgment, only a small proportion of the oxygen which passes from slag actually penetrates deep into the metal.

The following is cited in support of this theory.

In the first place, the absence of a strict interrelation between the variations of carbon and oxygen concentrations in time and along the height is emphasized. However, this fact points only to the complexity of the combustion process and contributes nothing to the theory concerning the location of the reaction front at the metal-slag interface.

Secondly, an assumption is made that the contents of carbon and oxygen within the metal volume approaches equilibrium. Yet, it is not always so, as may be seen, for example, from fig. 242.

Thirdly, the favorable influence is underlined of the slag-metal interface on the development of the reaction. Yet, for the latter the influence of the other boundary, namely that of metal with the hearth bed, is not less if not more favorable.

Finally, total reaction, according to the data of these authors, proceeds with heat absorption and this is "in perfect agreement with the regularity of the growth of decarbonization rate with increasing bath temperature as observed in practice." This conclusion is also wrong, since almost any reaction, whether exothermic or endothermic, accelerates with growing temperature.

Thus the arguments produced by Stark and Chelishchev are insufficient for the negation of bottom boil. The latter takes place most frequently after intensive heating of metal, at moderate carbon concentration and a favorable condition of the hearth bottom.

As a rule, it is accompanied also by the development of the reaction in volume, i.e., at the surface of the CO bubbles. This is evidenced by the "deoxidizing" effect of carbon dioxide blown through the metal, as well as by some of the curves pertaining to oxygen distribution along the cross-section of the bath.

One of the decisive arguments corroborating the existence of bottom ebulition is constituted by the slowing down of the decarbonization process in proportion to the slagging of the hearth bed.

KINETICS OF REACTION BETWEEN CARBON AND OXYGEN DISSOLVED IN METAL

The practical impossibility of spontaneous formation of CO bubbles in steel which does not contain sonims will be demonstrated later in the discussion of the bubble-metal equilibrium. Here the assumption is made that the bubbles have already emerged and the discussion is confined solely to the growth of the existing bubble-nucleus.

There are grounds to believe that the intensity of the total process of decarbonization is limited by the rates of interphase crossings at

the boundaries of metal with slag and with the bubble. Most essential among them are the inequations referred to earlier.

$$[O]_{sl} > [O]_{bub} > [O]_{C}. \qquad \text{(VIII, 322)}$$

They bear witness to the fact that steel is -- on the one hand -- peroxidized with regard to carbon dissolved in it, and -- on the other hand -- insufficiently oxidized with respect to slag. These interrelationships become comprehensible if one assumes that the stages limiting the flow of the process are constituted by heterogeneous processes at the boundaries of metal with bubble and with slag.

As to the stage of homogeneous chemical transformation

$$C_{(met)} + O_{(met)} = CO_{met},$$

to which reference has been made by many investigators (for instance [203], [204], [205]), its existence is highly questionable. The absence of CO molecules in liquid steel speaks against this theory.

It was repeatedly indicated that the chemical reaction of carbon oxidation bears a heterogeneous character as it develops at the metal-bubble boundary, and is tightly connected with the event of carbon monoxide desorption. In other words, the atoms of carbon and oxygen dissolved in iron form a CO molecule only at the bubble interface, whereupon it passes immediately into the gaseous phase.

The fact that CO molecules are absent in metal was disregarded for a long time by many investigators [198], [42], [206]. Attempts were therefore made by them to accomplish a kinetic analysis of decarbonization process in the assumption of the development of a homogeneous reaction of CO formation. In a number of cases, it was surmised that the intensity of the process is limited by the stage of CO molecule diffusion towards the surface of the growing bubble.

This theory will not be discussed below as totally groundless. Greater attention is due to the theories based on the surface character of the reaction.

CARBON OXIDATION BY AIR

According to Schwartzmann, Samarin, and Temkin [151], [106], the oxidation of carbon, sulfur, silicon, and manganese by oxygen has a diffusion character. Its intensity is determined by the rate at which these elements are supplied from the metal volume to its surface.

The kinetic characteristics of metal decarbonization as defined by them are close to those of the Bessemer process. The rate constant of the latter, calculated from industrial data and related to the unit of specific area, is equal to $29 \cdot 10^{-3}$, whereas the constant determined in experimental runs in a small induction furnace amounts to $30 \cdot 10^{-3}$.

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The above coincidence indicates the related character of the processes and emphasizes only the fact that they are both heterogeneous. In other words, the formation of CO molecules occurs here not in the volume of metal but at its interface with gas. This surface process requires the simultaneous presence of carbon and oxygen atoms at the interphase boundary. Moreover, direct interaction of carbon particles with the oxygen molecule is hardly probable. The solid bonds between the atoms of the latter must be considerably weakened beforehand. This takes place during chem-adsorption of oxygen on iron.

In connection with the foregoing, it seems to be doubtful indeed that there should not appear an extremely thin layer of liquid iron oxides at the surface of the metal. It must isolate iron to some degree or other from immediate contact with gas. Neither the circulation of metal, nor -- and even less so -- an attempt to clear its surface by means of a rod, can prevent it from being practically immediately recoated by a fresh film of iron oxides[1]. The same, apparently, occurs during blowing.

These circumstances, it seems, draw the process in question closer to that of carbon combustion in open-hearth furnace. Even the equation proposed by Schwartzmann, Samarin, and Temkin coincides in its form with the one derived in 1901 for the rate of decarbonization which was subsequently confirmed by the data resulting from smelting by ore process carried out at the Nadezhdinsky plant [207].

It is true that in the case of air oxidation the integumentary layer of "slag" is very thin. Local fractures of the oxide film and direct evolution of CO into the furnace atmosphere are possible. However, regardless of this, the C and O atoms present at the surface are the participants in the reaction.

If one assumes the rate of oxygen chem-adsorption to be very considerable, then the process may be interpreted as that of reduction of the Fe_xO_y monomolecular "protective" film by the atoms of carbon. Actually, experiments show [208] that the rate of interaction of liquid cast-iron with molten iron oxides (FeO and Fe_3O_4) conforms to the equation of the first order. It is true though that these measurements cannot be considered as reliable.

Be that as it may, the essential fact here is still that in the surface reaction zone the concentration of oxygen is many times higher than that of carbon. Hence, an equation of the first order may be obtained not only because of the insufficient rate of carbon diffusion, but also in consequence of the deceleration of the chemical act itself (VIII, 288')

$$C_{(met.surf)} + O_{(met.\ surf)} = CO_{(gas)}$$

Indeed, the reaction velocity v will then be determined solely by carbon since the quantity $(O)_{surf.}$ is practically constant

1 See also Part I, page 395.

$$v = k\,[C]_{surf}[CO]_{surf.} \qquad \text{(VIII, 323)}$$

Moreover a number of facts contradict the diffusion character of the process of oxidation by air of carbon contained in metal.

Listed among them should be the high coefficient of carbon diffusion in iron, the negligible irregularity of carbon distribution in the bath of open-hearth furnace, and the weak dependence of the rate of oxidation on the concentration of carbon. It is not proportional to the value of [C].

Experiments with air and oxygen blowing of metal show [175] that the rate changes relatively slowly with carbon contents, for example, in proportion to log [C] or according to a more complex law (fig. 243). Schwarzmann also seems to be inclined to accept this theory at the present time.

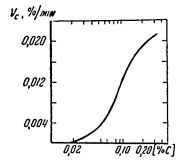

Fig. 243. Decarbonization velocity versus carbon contents in metal.

The weak dependence of the reaction velocity v upon [C] is apparently attributable to the fact that carbon constitutes a strong surface-active component in iron. A proportionality between the values of $[C]_{surf}$ and [C] exists only when the percentages of carbon in the volume are small. As a rule, the value of $[C]_{surf.}$ changes far less rapidly than that of [C] at medium volume concentrations of carbon.

Thus, experiments on carbon oxidation by air and oxygen indicate that this process has no diffusion character and is, apparently, determinable by the progress of heterogeneous reaction (VIII, 288').

The low temperature dependence of the velocity of oxidation calls for additional experimental proofs[1].

1 According to [208], the rate of liquid cast-iron reaction with iron oxides is very sensitive to temperature (activation energy 37,000 - 43,000 cal/mol). These data also call for verification (variable interface area between the phases, rise of the oxide temperature during heating, etc.).

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This is also required because the rise of temperature in induction furnaces is achieved by increasing strength of current. This, in turn, provokes intensive stirring of metal, i.e., facilitating carbon diffusion. Hence, even if the intensity of the process were limited by diffusion, it still would be reasonable to expect a fairly strong acceleration of interaction with growing temperature (and, consequently, also of the bath mixing).

ON THE POSSIBILITY OF OTHER REACTIONS

According to Schwartzmann, the burn-out of carbon contained in metal under the influence of oxidizing slags is subordinated to the same relationships as those governing its oxidation in air. In both cases, a proportionality is observed between the velocity of the process and the concentration of carbon. Moreover the rate constants also prove to be approaching each other. These circumstances induced him to assume again that the limiting process is constituted by carbon diffusion towards the reaction front.

Observations of carbon monoxide bubbles indicate that the reaction front is situated within the metal near the hearth bottom and not at the interface with slag. By what means then can rapid supply of oxygen be assured there if it is known that the coefficient of oxygen diffusion is appreciably lower than that of carbon diffusion? A very dubious surmise is furnished, by way of an answer to this question, to the effect that carbon monoxide penetrates from slag to the hearth through the capillaries of the refractory lining.

This process could hardly be faster than oxygen diffusion in metal, powerfully mixed by evolving CO.

The fact is also disregarded that the passage of O^{2-} and Fe^{2+} ions from slag to steel is a relatively slow process and it is assumed that the following reactions develop near the bottom

$$FeO_{(sl)} + C_{(met)} = Fe_{(met)} + CO_{(gas)}, \qquad \text{(VIII, 288')}$$

$$CO_{(gas)} + FeO_{(met)} = Fe_{(met)} + CO_{2\,(gas)}, \qquad \text{(VIII, 324)}$$

$$CO_{2\,(gas)} + C_{(met)} = 2\,CO_{(gas)}. \qquad \text{(VIII, 325)}$$

Analogous conjectures pertaining to the pattern of the process developing at the bubble surface were also expressed before [209]. Moreover[1], it was assumed that along with reaction (VIII, 288)

$$C_{(met)} + O_{(met)} = CO_{(bub)},$$

there develop two other reactions according to equations

$$CO_{(bub)} + O_{(met)} = CO_{2\,(bub)}. \qquad \text{(VIII, 324')}$$

$$CO_{2\,(bub)} + C_{(met)} = 2\,CO_{(bub)}. \qquad \text{(VIII, 325)}$$

However, such assumptions seem hardly justified. The slow progress of reaction (VIII, 325), which hampers the study of equilibrium between liquid steel and gaseous CO_2, is well known. At any rate, the velocity of this interaction is considerably lower than that of reactions (VIII, 324) and (VIII, 324').

But one should expect then that the bubbles which form in the bath contain almost pure carbon dioxide. This, however, is not the case. The presence of an appreciable content of CO_2 in gas given off by the bath is caused by another easily developing process, namely, by the reduction of ferrous oxide in slag by carbon monoxide.

The flow of reactions (VIII, 324) and (VIII, 324') is also impeded by conditions unfavorable for their equilibrium with metal. Actually, at 1600°C the gaseous phase at equilibrium may contain only 1% CO_2 when the concentrations of carbon are inferior to 0.2%. At higher carbon contents, the possible concentration of CO_2 becomes even smaller.

The experiments conducted by Andreyev and Yavoysky with pure carbon dioxide blowing through metal are also in conflict with the noticeable development of the additional reactions advanced in Schwartzmann's study and in work [209]. About 3 m³ CO_2 were introduced into an electric furnace with 10-ton capacity. The result was that the degree of metal oxidation not only failed to grow, but actually dropped somewhat (on the average of 0.015% FeO) while 0.33 kg of oxygen were released from the bath.

Thus blowing with pure carbon dioxide does not contribute to the development of reaction (VIII, 325) from left to right and of interactions (VIII, 324) and (VIII, 324') from right to left. It increases only the area of the metal-bubble interface assuring thereby a broader front for the progress of reaction (VIII, 288).

The foregoing as a whole permits one to think that the principal role in the process of metal decarbonization is played by interaction (VIII, 288). As to reactions (VIII, 325), (VIII, 324) and (VIII, 324'), these develop apparently on a very limited scale.

ON QUANTITATIVE RELATIONSHIPS

Many attempts have been made to determine the analytic dependence of the rate of carbon burn-out upon the principal conditions of the process development (Andreyev, Maksimov, Chuyko, Loerber, Larsen, and others). Yet they can hardly be considered successful. The fact is that the process under consideration is extremely complex from the point of view of kinetics. Its intensity is limited not by one but by several stages. Moreover, not all of them are defined with due conclusiveness.

[1] Major errors were made in study [209]. Thus, for instance, it is assumed that by dividing the volume of a gram-molecule of gas by Avogadro's number it is possible to determine the size of an individual particle. As a result of such erroneous calculations, an incredibly large radius of CO molecules was produced which is equal to 38 Å. It is obvious that postulates based on such foundations are groundless and require no discussion.

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On the basis of the afore-said, it is possible to cite the following stages which inhibit carbon burn-out. First of all, this is caused by diffusion of ions within slag, then by the passage of O^{2-} and Fe^{2+} from slag to metal and further by the heterogeneous reaction between carbon and oxygen.

Along with the mentioned stages, it seems to be necessary to note the slow diffusion of oxygen towards the reaction front inside the metal. This is evident from the fact of the very uneven distribution of oxygen along the height of the bath. In addition to this, one should also consider another fact, namely that the coefficient of oxygen diffusion is appreciably lower than that for carbon.

Finally, a very important stage which could bring the process as a whole to a complete standstill is constituted by the event of bubble formation to which we shall duly refer later on.

It is obviously difficult to embrace in one equation such a large number of factors, the more so because their number may vary depending on concrete conditions. By virtue of this fact, all efforts to derive such a relationship were accompanied by certain simplifications of the problem. The surface character of the carbon-oxygen reaction was more often disregarded, as well as the slow-down in the passage by O^{2-} and Fe^{2+} ions of the metal-slag boundary.

In view of this, instead of surface carbon and oxygen concentrations, volume concentrations of the same were introduced into velocity equations, i.e., $[C]_{surf.}$ and $[O]_{surf.}$ were considered to be equal respectively to $[C]$ and $[O]$. On the other hand, the equilibrium contents of oxygen with slag was substituted for its actual contents at the slag boundary, whereby $[O]_{fact\ surf.}$ was identified with $[O]_{slag}$. All this makes the proposed equations so approximative and singular that there is hardly any sense in dwelling on them in greater detail.

In conclusion, we shall consider only one regularity observed in the tests. From fig. 238, it follows that with diminishing carbon concentration in metal the product m', pertaining to the factual contents of O and C in metal, tends to equilibrium.

At first glance, this appears to be very strange since this creates the impression that the process reaches equilibrium (accelerates) more rapidly when the concentration of one of the reacting substances is dropping. Nevertheless, this is not so, and the observed regularity can be explained rather easily.

With the conditions established, the velocity of the decarbonization process as a whole is equal to the intensity of each of the successive stages and, in particular, that of the reaction between carbon and oxygen

$$v = v_x = k_1[C]\ [O]\ - k_2 p_{CO.\,(bub)}. \qquad \text{(VIII, 326)}$$

At small contents of carbon and oxygen their surface concentrations become proportional to volume concentrations[1]

$$v = k_1 k' [C][O]_{p.ver} - k_2 p_{CO\,(bub)}. \qquad \text{(VIII, 327)}$$

By replacing p_{CO} in the expression for equilibrium conditions, we obtain

$$v = k\,[[C][O]_{p.ver} - [C][O]_{equil}], \qquad \text{(VIII, 328)}$$

whereupon

$$\frac{m'}{m} = \frac{[C]\,[O]_{fact}}{[C]\,[O]_p} = \frac{v}{k\,[C]\,[O]_p} + 1. \qquad \text{(VIII, 329)}$$

Whenever the concentration of carbon shows a tendency to vanish, the reaction rate also approaches zero. Nevertheless, the product

$$[C][O]_p = m$$

still continues to remain constant according to the law of mass action. Then the experimentally observed regularity results directly from equation (VIII, 329)

$$\left|\frac{m'}{m}\right|_{[C]\to 0} \to 1. \qquad \text{(VIII, 330)}$$

EQUILIBRIUM OF BUBBLE AND METAL

PURE CARBON MONOXIDE

The equilibrium of carbon monoxide with liquid steel was discussed earlier for the case when the phase boundary is flat. The matter becomes somewhat more complicated when the CO bubble is in equilibrium with metal. In this case, its dimensions and its location within the bath should be taken into account.

Actually the pressure of carbon monoxide inside the bubble, as mentioned repeatedly by a number of authors, in particular by Dobrokhotov and Andreyev, is determined by equation

$$p_{CO} = P_a + h_{(sl)}\gamma_{(sl)} + h_{(met)}\gamma_{(met} + \frac{2\sigma}{r} \qquad \text{(VIII, 331)}$$

wherein P_a = atmospheric pressure;
h_i and γ_i = height of the column and specific gravity of slag and steel;
σ = surface tension; r = radius of bubble.

[1] This apparently explains the fact that equation (VIII, 327) while agreeing with experimental values when the reaction rates are small [210], loses its validity when the contents of carbon are elevated [175].

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By combining the first three addends, we have

$$p_{CO} = P_0 + \frac{2\sigma}{r}. \qquad \text{(VIII, 332)}$$

Formula (VIII, 332) permits the calculation of the CO pressure in a bubble which has a definite size and is located at any given level in the bath. The knowledge of p_{CO} value is important for the clarification of the question concerning the thermodynamic stability of the bubble. As is well known, the latter depends on the sign of ΔF, while for a general case

$$\Delta F = RT(\ln \prod_i a_i - \ln K_3). \qquad \text{VIII, 333)}$$

When the activities of carbon and oxygen are given, equation (VIII, 333) assumes a more simplified aspect

$$\Delta F = RT(\ln p_{CO,r} - \ln p^{\circ}_{CO,r}). \qquad \text{(VIII, 334)}$$

Whereupon it follows that the bubble and metal reach a state of equilibrium when

$$\ln p_{CO,r} \quad \ln p^{\circ}_{CO,r}. \qquad \text{(VIII, 335)}$$

If the phase interface is flat, the equilibrium constant of reaction (VIII, 288) may be recorded as follows

$$K_3 = \frac{p^{\circ}_{CO,\infty}}{a_C \cdot a_O}. \qquad \text{(VIII, 336)}$$

Since the surface boundary of the bubble is concave, the equilibrium pressure here should be different, namely

$$\ln p^{\circ}_{CO,r} = \ln p^{\circ}_{CO,\infty} - \frac{2\sigma M_{CO}}{RTr\gamma_{CO}}. \qquad \text{(VIII, 337)}$$

Here M_{CO} = molecular weight of CO;
γ_{CO} = density of gas;
r = radius of bubble.

By combining equations (VIII, 332), (VIII, 335), (VIII, 336) and (VIII, 337) we find

$$\ln\left(P_0 + \frac{2\sigma}{r}\right) = \ln K_3 + \ln(a_C \cdot a_O) - \frac{2\sigma M_{CO}}{RT\gamma_{CO}}. \qquad \text{(VIII, 338)}$$

This equation permits one to determine the stable size of the bubble if the following data are known: pressure P_0 at the bath level under consideration, temperature, and composition of steel (% C and % O). Such bubble radius is called critical. A bubble with a critical radius does not contract (or dilate) under the influence of the forces of external pressure, and, in addition to this, it does not react with metal, i.e., it is not only mechanically, but also chemically, at equilibrium with metal.

Indeed, if for some reason the bubble radius turns out to be smaller than critical, i.e., if $r < r_{cr}$, then equation (VIII, 338) would be upset. Its left part $\left[\ln p_{CO,r} = \ln(P_0 + \frac{2\sigma}{r})\right]$ would increase, since P_{CO} is inversely proportional to r, while the right part would diminish because of the growth of the subtrahend. In other words, actual pressure in the bubble would be greater than is required by the conditions of equilibrium for reaction (VIII, 288)

$$C_{(metal)} + O_{(metal)} = CO_{(bubble)},$$

i.e.,

$$p_{CO,r} > p^{\circ}_{CO,r}.$$

According to equation (VIII, 334) this means that $\Delta F > 0$ and the bubble is unstable. Its size will diminish as a result of the passage of gaseous CO into metal in the form of C and O atoms as per reaction (VIII, 288). The latter must proceed from right to left which will cause a still greater decrease of r, the growth of $\Delta F > 0$, and, in the final count, this will lead to the solution in metal of the entire available carbon monoxide, resulting in the disappearance of the bubble.

On the contrary, if the bubble's size is greater than critical, i.e., if $r > r_{cr}$, then equation (VIII, 338) would be upset because $\ln p_{CO,r}$ would become smaller than $\ln p^{\circ}_{CO,r}$. Since in this case $\Delta F < 0$, a spontaneous progress of reaction (VIII, 288) from left to right becomes possible. The bubble radius will grow, assuring the successful development of decarbonization.

The foregoing is illustrated in fig. 244. Here, for different r, the values are given of p_{CO} which correspond to mechanical equilibrium as per formula (VIII, 332) and to chemical stability according to formula (VIII, 337). The point of intersection of these curves corresponds to the critical parameters of the bubble.

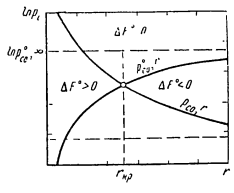

Fig. 244. Effect of the bubble size on p_{CO}, corresponding to mechanical ($p_{CO,r}$) and chemical ($p^{\circ}_{CO,r}$) equilibrium with metal.

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MIXTURE OF TWO GASES

On the basis of somewhat different considerations, it is possible to come to similar conclusions with regard to the existence, under given conditions, of bubbles of a stable size.

The change of free energy during the formation of a bubble is equal to its increment caused by the passage of particles from one phase into another (from chemical potentials of C and O to the potential of CO), plus the work needed for the formation of a new surface

$$\Delta F = (\mu_{CO} - \mu_C - \mu_O) n + \alpha n^{2/3}. \qquad \text{(VIII, 339)}$$

Here the addend $4\pi r^2 \sigma$ is assumed to be equal to $\alpha n^{2/3}$.

So long as the difference between the chemical potentials is positive, the magnitude of $\Delta F > 0$, and the probability of the formation of a bubble (or the number of such bubbles)

$$N = Ae^{-\frac{\Delta F}{RT}} \qquad \text{(VIII, 340)}$$

will be the lesser, the greater the number of CO particles in it, i.e., the greater the value of n.

In the other hand, if $\mu_{CO} < \mu_C + \mu_O$, then ΔF will initially increase with growing n, but will begin to fall later (fig. 245). The maximum of ΔF corresponds to the size of bubble which can also be called critical. Indeed, its further growth could proceed spontaneously since the growth of n in excess of n_{cr} causes a decrease of ΔF.

Recently Nesis and Frenkel [211], proceeding along these lines, examined a more complex problem when the bubble is formed by two gases, namely by vapors of the solvent and the dissolved substance. Having designated the number of molecules of the first and second component in the bubble by n' and n'', and their chemical potentials in both phases by μ_1', μ_1'', μ_2' and μ_2'' they composed an expression for the change of free energy

$$\Delta F = (\mu_2' - \mu_1') n' + (\mu_2'' - \mu_1'') n'' + 4\pi r^2 \sigma. \qquad \text{(VIII, 341)}$$

Assuming that the liquid composition remains constant, while replacing the chemical potentials of the components in the bubble by means of equations

$$\mu_2' = \mu_{2,0}' + kT \ln \frac{n'}{n' + n''}, \qquad \text{(VIII, 342)}$$

$$\mu_2'' = \mu_{2,0}'' + kT \ln \frac{n''}{n' + n''}, \qquad \text{(VIII, 343)}$$

we find

$$\Delta F = (\mu_{2,0}' - \mu_1') n' + (\mu_{2,0}'' - \mu_1'') n'' + kT\left(n' \ln \frac{n'}{n' + n''} + n'' \ln \frac{n''}{n' + n''}\right) + 4\pi r^2 \sigma. \qquad \text{(VIII, 344)}$$

By equating further

$$4\pi r^2 \sigma = \alpha (n' + n'')^{2/3}, \qquad \text{(VIII, 345)}$$

and designating

$$\mu_{2,0}' - \mu_1' = -A, \qquad \text{(VIII, 346)}$$

$$\mu_{2,0}'' - \mu_1'' = -B, \qquad \text{(VIII, 347)}$$

we obtain

$$\Delta F = -An' - Bn'' + \alpha (n' + n'')^{2/3} + kT\left(n' \ln \frac{n'}{n' + n''} + n'' \ln \frac{n''}{n' + n''}\right). \qquad \text{(VIII, 348)}$$

This formula is represented in fig. 246 by a surface with a double curvature. Its plane projection may be composed of three fields. In the conditions of the first (I), where

$$\frac{\partial \Delta F}{\partial n'} > 0 \quad \text{and} \quad \frac{\partial \Delta F}{\partial n''} > 0, \qquad \text{(VIII, 349)}$$

the bubble is unstable and dissolves in the liquid phase.

On the contrary, for field III, where

$$\frac{\partial \Delta F}{\partial n'} < 0 \quad \text{and} \quad \frac{\partial \Delta F}{\partial n''} < 0, \qquad \text{VIII, 350)}$$

As to the region II, here

$$\frac{\partial \Delta F}{\partial n'} > 0 \quad \text{and} \quad \frac{\partial \Delta F}{\partial n''} < 0,$$

or vice versa. In other words, the bubble is stable at times with respect to the first component, at others with regard to the second. Hence, depending on concrete conditions, both the growth and the disappearance of the bubble are possible.

The above procedure outlines the general course for the study of the behavior of bubbles formed by several components. This takes place almost always during decarbonization of steel. In this case, apart from CO, other substances dissolved in metal, such as hydrogen and nitrogen, for example, also penetrate into the bubble.

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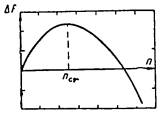

Fig. 245. Schematic diagram illustrating the effect of the number of particles in the bubble nucleus on the change of free energy during its formation.

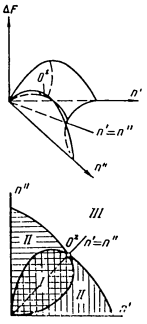

Fig. 246. Effect of the particles of the first (n') and second (n'') components on the change of free energy during the formation of the bubble nucleus.

0* -- synclinal point

ON THE POSSIBILITY OF BUBBLE FORMATION IN LIQUID STEEL.

From the foregoing, it follows that a gas bubble formed in liquid is capable of further development only in case that its radius attains the critical size. Bubbles of smaller size, like crystal nuclei, are unstable and dissolve again in the liquid phase.

The critical bubble radius is very sensitive, as follows from equation (VIII, 338), to the magnitude of surface tension σ and the degree of supersaturation of the liquid. According to Andreyev [193] the effect of these factors may be represented by the data listed in table 41.

Since surface tension of iron is close to 1500 erg/cm^2 [212], [213], then for the internal open-hearth bath levels the penultimate line in table 41 is most interesting.

It follows therefrom that in these conditions the critical radius of the bubble is relatively large and is measured in hundredth fractions of 1 millimeter.

Table 41

The number of CO molecules in a bubble of critical size depending on conditions

σ erg/cm^2	External pressure atm.	Critical radius r·10^3, cm, at supersaturation p_∞/p^0						Number of molecules in bubble at supersaturation equal to 8	$\exp\left\{\frac{4\pi r_{cr}^2\sigma}{3kT}\right\}$
		1.1	1.5	2.0	4.0	6.0	8.0		
70	1.0	2.85	0.59	0.31	0.11	0.07	0.05	$4.98 \cdot 10^7$	$10^{-8.3 \cdot 10^6}$
900	1.35	27.2	5.66	2.99	1.07	0.66	0.48	$0.94 \cdot 10^{10}$	$10^{-1.46 \cdot 10^{10}}$
1500	1.35	45.2	9.42	4.91	1.77	1.10	0.80	$4.16 \cdot 10^{10}$	$10^{-6.7 \cdot 10^{10}}$
2000	1.35	60.3	12.6	6.56	2.36	1.47	1.07	$10.1 \cdot 10^{11}$	$10^{-16.2 \cdot 10^{11}}$

Its formation is connected with the accumulation at a given point of a considerable number of molecules (of the order of 10^{10} units). A spontaneous materialization of this event is hardly probable, since this requires (in view of the absence of CO molecules in steel) a similar isochronal concentration of carbon and oxygen atoms within a small volume of metal.

Indeed, the probability of the system's free energy fluctuation by the magnitude of ΔF is expressed through equation

$$P = Ae^{-\frac{\Delta F}{kT}}. \qquad \text{(VIII, 351)}$$

Here A is approximately equal to the total number of molecules. Its order of magnitude varies from 10^{10} to 10^{30}. The magnitude of ΔF, in case of nucleus formation, is measured by one third of its surface energy

$$\Delta F = {}^1/_3 \cdot 4\pi r^2\sigma. \qquad \text{(VIII, 352)}$$

As may be seen from the last column of table 41, the ratio $\frac{\Delta F}{kT}$ is quite large, in consequence of which the probability of the bubble formation, according to expression (VIII, 351), approaches to zero.

It should be noted that such conclusions relate to conditions most propitious for the formation of bubble nuclei.

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For smaller supersaturations the value of r_{cr} increases while the probability of bubble formation diminishes. This precludes the possibility of spontaneous formation of a stable carbon monoxide bubble within the volume of pure liquid steel.

This conclusion is also confirmed by the results of an analysis of the possible and necessary degrees of supersaturation. According to Andreyev's calculations, the possibility of spontaneous formation of a CO bubble in the bath becomes mensurable when, at $\sigma = 900$ erg/cm^2, the critical radius decreases to the magnitude of the order of 10^{-7} cm. Such r_{cr} values are only possible in case of extreme supersaturation of metal with respect to carbon monoxide. After Andreyev, supersaturation must comprise 3800 and $p^{o}_{CO,\infty} = 5130$ atm which in inconceivable under normal conditions.

Actually the supersaturation of an open-hearth bath with respect to CO is small, as a rule. According to the data of a number of investigators [8], [160], [198], [204], the concentrations of carbon and oxygen in metal are such that they are apt to remain in a state of equilibrium with gaseous CO which has a pressure $p^{o}_{CO,\infty} = 1.5 - 5.0$ atm. Such small supersaturation (2-3 times) makes it absolutely impossible for a spontaneous formation of bubbles to occur in pure liquid steel.

The afore-said may be substantiated not only by calculations but also by experimental data. Examples of superheating of pure, degasified liquids in vessels with well-fused walls may be found, for example, in the Physics Textbook by Hvolson [214]. As a matter of fact, he reports data pertaining to the possible superheating of water up to 200°C at a pressure of 1 atm. It is observed thereby that the introduction of coarse bodies facilitates gassing.

The same may be said not only of the boiling of organic or aqueous solutions, but also of ebulition resulting from chemical reaction in liquid.

For metals, the surface tension of which is tens of times greater than that of aqueous solutions, these obstacles are obviously even greater [see equation (VIII, 351)]. The question arises then -- what causes the evolution of CO in open-hearth baths with supersaturations thousands of times less than anticipated (see table 41)?

The answer to this question is provided by the analysis of the effect of solid bodies on the probability of nuclei formation.

EFFECT OF THE SURFACE OF SOLID BODIES ON THE FORMATION OF BUBBLES

It is common knowledge that bubbles appear during de-gasification not in the volume of liquid, but in places where it comes into contact with solid bodies. For example, cold tap water poured into a vessel proves to be supersaturated with air because its temperature has increased while the pressure dropped. Evolution of gas from it begins with the formation and growth of bubbles on the walls of the vessel.

The same phenomenon is to be observed during ebulition of liquid. Vaporization is concentrated over the surface of solid bodies. Boiling without too high a degree of superheating occurs in containers with coarse surface or during introduction into the liquid of porous bodies, capillaries, etc.

All these and many other observations indicate that the presence of solid, and particularly porous, bodies facilitates substantially the emergence of the nuclei of the new phase. This effect is based on the circumstances discussed in Chapter II dealing with crystallization.

CAUSES OF THE EFFECT

During the formation of a bubble on a smooth horizontal surface, its shape is determined by the interrelationship of interphase tensions at the solid body's interfaces with liquid (σ_{s-l}) and with gas (σ_{s-g}), as well as that of gas with the liquid (σ_{l-g}).

Two alternatives are possible here (fig. 247). In the first case the liquid wets the solid body better than gas ($\sigma_{s-g} > \sigma_{s-l}$); in the second instance the reverse is true, i.e., $\sigma_{s-g} < \sigma_{s-l}$. Case (1) corresponds to the acute angle of moistening ($\theta < 90^{\circ}$). Here the bubble is characterized by the presence of a specified diameter. On the contrary, for case (2) the angle O is obtuse, and the bubble has a lenticular form.

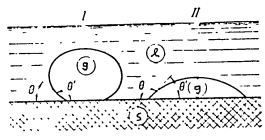

Fig. 247. Shapes of bubbles formed on the horizontal surface of a solid body.

I -- Liquid moistens the solid body better than gas;
II -- Gas moistens the solid body better than liquid.

The relationship between surface tension and the rim angle is provided, as is well known, by Neumann's equation

$$\sigma_{ls} = \sigma_{sg} - \sigma_{lg} \cos\theta \qquad \text{(VIII, 353)}$$

or

$$\cos\theta = \frac{\sigma_{sg} - \sigma_{ls}}{\sigma_{lg}} \qquad \text{(VIII, 354)}$$

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As shown by Aron and Frenkel [215], [216], expressions (VIII, 353) and (VIII, 354) are valid only in the particular cases when the underlying solid surface is homogeneous along the entire perimeter of phase contact, and when the bubble (or bead) is located on a horizontal plane. The effect of a coarse lining will be discussed later.

As to the second condition, an unsymmetric form of the bubble (bead) with a variable angle θ is characteristic for a non-horizontal surface. Responsible for such a shape is the influence of the gravitational forces (fig. 248). This phenomenon is to be observed at the batters of the furnace. Moreover, the bubble may rise and the bead may roll down when a definite critical mass is attained.

The latter may be determined from the relationship

$$\sin\alpha = 2r\frac{\Delta\sigma}{mg}, \qquad \text{(VIII, 355)}$$

where r is the radius;
m - the mass of the bubble (bead);
$\Delta\sigma = \sigma_{s\text{-}g} + \sigma_{l\text{-}g} - \sigma_{s\text{-}l}$ is the energy of adhesion;
g - acceleration of terrestrial gravitation.

Hence

$$m_{min} = \frac{2r\Delta\sigma}{g}. \qquad \text{(VIII, 356)}$$

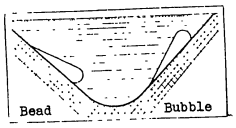

Fig. 248. Schematic diagram of a bead sliding down and a bubble rising up the sloping surface.

The shape of the bubbles and beads, located on a horizontal surface (see fig. 247) and remaining at equilibrium with a liquid which does not chemically interact with them, has been studied by a number of authors.

The general differential equation covering that part of the bead surface upon which, in view of its remoteness, no influence of the lining material is reflected (case I, fig. 247), has the following aspect

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{\Delta d}{\sigma}x + \frac{2}{R_0}. \qquad \text{(VIII, 357)}$$

Here R_1 and R_2 - are the main curvature radii of each point of the surface;
Δd - is the difference between the densities of the contacting phases (with the exception of the solid);
σ - is interphase tension ($\sigma_{l\text{-}l}$ or $\sigma_{l\text{-}g}$);
x - is the vertical distance from the point to the vertex of the bead;
R_0 - is the curvature radius at the vertex.

This equation is valid for the surface of the bead removed from the area of contact between the liquid and the solid body. It takes into account only forces of gravity and surface tension. For purposes of practical application it is convenient to integrate it graphically [217], [218].

Formula (VIII, 357) is also true for the bubble surface. In this case, however, the quantity Δd will be negative.

To characterize the shape of the bubble, Nesis [219] used Frenkel's solution [220] produced for a bead situated upon a horizontal surface. The integral aspect of this equation is as follows

$$\sin^2\frac{\theta}{2} = \frac{1}{4a^2}(h^2 - y^2) + \lambda(y - h), \qquad \text{(VIII, 358)}$$

where y - is the ordinate of the bubble's contour;
h = y_{max} - is the height of the bubble in the center;
λ - is Lagrangian indefinite factor;
$a^2 = \frac{\sigma_{l\text{-}g}}{\rho g}$ - is the parameter having the dimensionality of the square of the length;
ρ - is density;
g - gravity acceleration.

Equation (VIII, 358) is interesting in that it illustrates the change of the bubble's shape during its growth up to the moment of its take-off.

Fig. 249. Diagram showing the growth of bubble located on the surface of a solid body.

Actually, with its aid it is possible to demonstrate that the growth of the bubble under the influence of Archimedean forces causes a gradual expansion of angle θ and progressive necking-in of the bubble (fig. 249) resulting in its breakaway. This occurs when the lifting force becomes

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equal to the forces of cohesion along the neck. After the take-off of the main gas mass, there remains a small lenticular bubble at the surface of the solid body.

The foregoing also takes place in case II when $\theta > 90^\circ$. Once a bubble is formed here, it will always be leaving a nucleus behind upon take-off. This removes the obstacles referred to above to the passage of carbon and oxygen atoms into the gaseous phase.

Moreover, the solid surface not wetted by metal ($\theta > 90^\circ$) does not only preserve the nuclei left behind by bubbles, but also facilitates the emergence of new ones. This is due to the fact that the curvature radius of the lenticular bubbles may attain considerable values even if the volume of gas is very small. Consequently, in this case the capillary pressure decreases. In other words, a far smaller amount of molecules may produce a nucleus of critical size here than in the case of a spherical bubble. All this contributes substantially to the process of nuclei formation.

In addition to this, the selective adsorption of gas molecules on the surface of the solid body not moistened by liquid ($\theta > 90^\circ$) will also facilitate the emergence of bubbles. It is especially strong for an uneven contact surface with a highly broken relief.

Indeed, the change of free energy ΔF during the formation of a gaseous phase nucleus upon a solid surface

$$\Delta F = {}^1/_3(\sigma_{l_g} S_{g_3} + \sigma_{s_9} S_{s_9} - \sigma_{l_s} S_{l_s}). \qquad \text{(VIII, 359)}$$

Assuming as a first approximation that the surface of the nucleus is a section of the sphere, upon introduction of angle θ (see equation /VIII, 354/) we obtain

$$\Delta F^\circ \cong \frac{1}{3}\sigma_{l_g} S_{l_3}\left(1 + \cos\theta + \operatorname{ctg}^2\frac{\theta}{2}\right). \qquad \text{(VIII, 360)}$$

From this expression it transpires that with the growth of angle θ, i.e., with increasing adhesion between gas and the solid body, the parenthesized quantity will diminish. Hence, if the surface area S_{l-g} is fixed, the variation of free energy ΔF will drop. This implies an increasing probability of heterophase fluctuation assuring the formation of a stable bubble. The reduction of surface tension of metal should lead to the same result.

A different picture arises when the solid body is wetted by liquid ($\theta < 90^\circ$). In this case there appear relatively small almost spherical bubbles which leave no nuclei on the surface upon take-off. This is to be attributed to the fact that for $\theta < 90^\circ$ the work needed for the breakaway of the entire bubble is smaller than that required for its partial separation. In addition to this, the low effectiveness of such smooth surfaces is also due to the considerable curvature of the particles which increases substantially the equilibrium pressure $p_{CO,r}$.

EFFECT OF WETTING

Let us review a few experimental data which illustrate the foregoing. First of all, it was repeatedly established that the volume V of the separating bubble is greater, the less the solid body moistened by liquid. In other words the value of V grows together with the rim angle θ.

Fig. 250. Diagrams of photographs of bubbles with different rim angles θ before separation from the electrode:

a -- $\theta = 18^\circ$; b -- $\theta = 75^\circ$; c -- $\theta = 97^\circ$ (magnified 6 times).

Fig. 250 reproduces photographs /221/ of bubbles before take-off from an electrode for θ = 18, 75 and 97°. As may be gathered from the diagram, their size increases with θ.

The conditions and the peculiarities of the boil of liquid heated from underneath a horizontal surface was studied with the aid of films /222/. Fig. 251 confirms that, depending on the wettability of the lining, the shape and the size of the bubbles change as described above. It was established that the separation of the first type of bubble ($\theta > 90^\circ$) occurs as a result of necking-off while a ready nucleus remains on the surface of the solid body. This was not observed in the case of moistened surfaces, i.e., when the angle $\theta < 90^\circ$ /223/.

It is interesting to note that the growth of bubbles on a heated solid surface proceeds faster than after take-off. This may be explained by lesser superheating (and, consequently, also supersaturation) of the liquid volume as compared with the surface through which heat is being transmitted.

Similar observations were made by Andreyev /193/, /224/, /225/ concerning the existence of three types of bubbles -- as illustrated in fig. 251 -- depending on the wettability of the underlying surface. While carefully pouring off the aqueous solutions of acetic acid and soda, he established, in addition to the above, that in new glass vessels with well-fused walls no evolution of gas was to be registered. On the other hand, upon introduction of coarse particles or lumps not wettable by the solutions -- as well as in the case when the walls of the vessel were eroded -- a powerful evolution of CO_2 was observed. Gassing developed at the surface of the solid body.

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Fig. 251. Dependence of the vapor bubble on the wettability of the solid surface.

I -- not wettable; II -- poorly wettable; III -- wettable.

It is important to emphasize two facts here - first, intensification of ebulition on non-wettable surfaces ($\theta > 90^\circ$), the causes of which were considered above, and second, facilitation of bubble formation by coarse bodies which is to be discussed presently.

As is known, the intensity of boiling of open-hearth baths depends substantially on the condition of the hearth bed, and primarily on the degree to which it is slagged [156].

Of course, the drop of the carbon burn-out rate in proportion to the impregnation of the magnesite bed with slag is a complex phenomenon (a change occurs in the composition, the porosity of metal, etc.). Nevertheless, the fact is noteworthy that the wettability of the hearth by metal increases simultaneously and parallelly with this.

Similar observations were made by Sapiro [226], [227], Levin [228] and by other investigators. According to the former, the rim angle θ' for a bead of metal (0.7-1.14% C and 13.0-0.25% Mn) placed on a slagged and a clean magnesite body amounted, respectively, to

before slagging	128°	118°	125°	108°
after slagging	63°	84°	82°	69°

i.e., it dropped considerably during slagging.

Analogous results were produced by Leving for metals of different composition. He found, for example, that the average value of angle θ' for Armco-iron on unslagged magnesite comprised 126°. The value of θ' dropped to 104° after the lining was covered with ore or oxidizing slag, or even with reduction period slags.

Andreyev furthermore believes that the intensive bubbling developing around a metal rod dipped into the bath is to be attributed to the fact that it is poorly wetted by steel. This is possibly due to the absence of a direct contact between the atoms of Fe caused by the presence of scale.

The boil subsides when the rod becomes hot.

Thus the conditions for the formation of bubbles on flat poorly wetted surfaces are more favorable than in the volume of metal. Apart from this, an exceptionally high influence on the probability of bubble formation is produced by the relief of the solid surface.

EFFECT OF COARSENESS

How important is the role of porous and coarse surfaces for the process of decarbonization may be gathered, for example, from the following tests [229]. If during smelting of steel in a high-frequency induction furnace, through increase of power, a circulation is produced at which liquid slag isolates the metal from the walls of the crucible, then the evolution of gas slows down abruptly while the contents of carbon may become tens or hundreds of times greater than equilibrium.

Upon re-establishment of contact between steel and the refractory lining, resulting either from a reduction of the power input, or through destruction of the separating slag layer with the point of a quartz rod, intensive decarbonization may again be achieved.

The importance of the relief of the hearth bottom consists in that its coarseness changes the angle of wetting, while porosity is responsible for the preservation of the gaseous phase nuclei.

While speaking of coarseness, it seems worthwhile to draw a line of distinction between the macroscopic rim angle θ and the micro-rim angle θ_0. There exists the following relationship between them [230] which was theoretically substantiated by Deryagin [231]

$$\cos\theta = k\cos\theta_0 = \frac{S}{S_0}\cos\theta_0 . \qquad \text{(VIII, 361)}$$

Here S and S_0 - are the true and the apparent surfaces of the solid body;

k - is the coefficient of coarseness.

Sometimes use is made of expression

$$k = \frac{1}{\overline{\cos\beta}}, \qquad \text{(VIII, 362)}$$

in which $\overline{\cos\beta}$ is the mean value of the cosine of the steepness of the micro-relief.

Deryagin also specified the limits of the applicability of relationship (VIII, 361). It is valid when the height and the distance between the neighboring ridges of the micro-relief are small in comparison with the capillary constant and the radii of the meniscus macro-steepness near the walls. It is important too that the sphere of molecular action should possess a radius smaller than that of the micro-relief steepness, and that inequation $k\cos\theta_0 < 1$ be observed.

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It follows from equation (VIII, 361) that the rim angle increases with growing coarseness, i.e., that wettability decreases. This, in turn, facilitates the formation of bubbles.

The relationship between the rim angle and the coarseness of the lining has been confirmed experimentally by a number of authors [193], [228], [232], [233] both for low and for high temperatures. Table 42, by way of illustration, incorporates the data produced by Sapiro [226] for steel.

Table 42

Dependence of the rim angle on the coarseness of the surface.

Contained in steel, %		Rim angle θ, with magnesite surface	
C	Mn	coarse	smooth
1,14	0,13	150—153°	139—135°
0,15	0,50	162—170°	124°
0,16	0,50	151—157°	121—126°

It should finally be noted that in a number of cases the sharp ribs (ridges) of the coarse surface may appreciably reduce supersaturation required for the formation of bubble nuclei [193], [226], [227].

PORES WETTED BY LIQUID METAL

When the liquid is in contact with a solid body the pores of which contain at least a small quantity of gas, the formation of bubbles is greatly facilitated. When wettability is perfect, the metal surface will not only prove to be concave but its curvature radius r will be equal to that of the pore r_n (fig. 252). In other words, the gas contained within the pore volume constitutes a nucleus of a bubble which will be stable if $r_n \geq r_{cr}$.

Thus, in case of perfect wettability of the surface by metal, only those pores will become active whose radii are greater or equal to the radius critical for the bubble. This, of course, refers only to the pores not entirely filled with steel. If, for some reason or other, there is no gas in them at all, then such pores, regardless of their sizes, will remain inactive.

Conditions change somewhat when the lining is wetted by metal imperfectly ($0 < \theta < 90^0$). In this case

$$r_{n.\,kp} = r_{kp} \cdot \cos\theta, \qquad \text{(VIII, 363)}$$

i.e., the critical size of the pores increases with declining wettability (with the decrease of angle θ).

The maximum pressures of gas in the bubble take place apparently, until it still remains in the pore volume. After its emergence into the bath volume, the conditions of growth become more favorable.

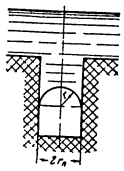

Fig. 252. Diagram of a pore partially filled with the liquid wetting the solid body.

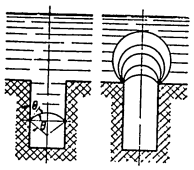

Fig. 253. Diagram of the growth of a bubble in a pore wetted by liquid.

Moreover, the take-off of the bubble will occur at the top of the pore (fig. 253). However, unlike the situation which develops in the case of a smooth surface where a breakaway at $\theta < 90^0$ leads to the liquidation of the nucleus, here there will remain a small amount of gas in the pore which will facilitate the subsequent formation of bubbles.

PORES NOT WETTED BY LIQUID METAL

In those cases when a porous solid body is not wetted by liquid metal, the surface of metal in the pore will be bulging towards the gaseous phase ($\theta > 90^0$). Such curvature assures better conditions for gas evolution than those characteristic for a smooth surface.

When $\theta > 90^0$ the gas pressure in the pore

$$p_r = p_{ext} - \frac{2\sigma}{r} \qquad \text{(VIII, 364)}$$

is smaller than external pressure (p_{ext}). For this reason in a supersaturated system there will develop a spontaneous growth of the gas volume in the pore. The liquid will be forced out from the capillary by gas.

Upon reaching the opening of the pore (fig. 254) the contact surface will become concave (III) instead of convex (I, II) with respect to gas, while retaining the same rim angle θ. Moreover, according to equation (VIII, 364) the changeover from position (I) to position (II) may occur under the influence of capillary forces even when gas pressure in the pore is inferior to external pressure. This is not the case when position (II) changes into position (III), since here the interface is flat at the initial moment.

Evidently, in this case, the growth of the bubble and the passage of the contact surface into a position with a stable rim angle ($\theta > 90^0$)

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are possible only when the metal is supersaturated with carbon and oxygen to a degree which corresponds to flat interface.

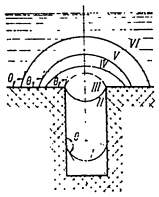

Fig. 254. Diagram of the growth of bubble in a pore not wetted by liquid.

Thus for unwettable linings all the pores unfilled by metal may serve as centers of degassing. If steel, at the beginning of reduction, was not supersaturated with gas, then the latter may dissolve while passing from the pores to metal. Steel will fill in the capillaries if their radius satisfies the following condition

$$r_n \geq \frac{2\sigma}{p_{ext}} \cdot \cos\theta . \qquad \text{(VIII, 365)}$$

As a result of this, such pores may become deactivated, i.e., they will not participate in the formation of bubbles during subsequent supersaturation of metal.

The growth of a bubble formed over a pore proceeds in the conditions of the existence of a constant angle θ[1] by means of gradual expansion of the contact perimeter of three phases (gas-hearth bottom-metal). The take-off of the bubble when $\theta > 90^0$ occurs in the same manner as in the case of a flat surface, i.e., only the upper part of the bubble separates. The balance -- its stem -- remains fixed to the solid body and serves as a center for the accumulation of new portions of CO.

In conclusion, it is important to state that both cases considered ($\theta < 90^0$ and $\theta > 90^0$) are limiting. The quantity θ does not remain constant during the melting process. Thus, for instance, according to Sapiro /226/ for freshly fritted lining, the porosity of which on the average approaches 6 - 7% /235/, the rim angle is obtuse, varying, as stated earlier, from 108 to 128°. Here the overwhelming majority of pores is active.

As the slagging of the hearth bottom proceeds the angle θ' decreases and drops to values considerably lower than 90°. In this case only those capillaries the radii of which satisfy equation (VIII, 363) become active. In view of this, the evolution of gas becomes inhibited and the process of decarbonization slows down.

1 For information on the hysteresis of the rim angle, see /193/, /231/ and /234/.

Together with the decrease of angle θ', i.e., along with diminishing activity of pores in the process of melting, their number also changes. According to Andreyev and Matyukha /225/ in the acid process decarbonization accelerates not only because of improved conditions of metal heating. The intensity of bubbling often rises also in consequence of the loosening of the upper layer of the hearth bottom as a result of reaction

$$SiO_{2(solid)} + 2C_{(melt)} = Si_{(melt)} + 2CO_{(gas)} .$$

Kramarov, in studying the behavior of metal in a crucible with acid lining, revealed a similar phenomenon. As ebulition develops, there forms in the surface layer of the crucible a network of capillaries which constitute the centers of gas evolution.

He noticed at the same time that the frequency of the emersion of bubbles is very low (5-8 per second) whereas the number of active pores is great (up to 2000). This seems to imply that in the conditions of Kramarov's tests, the evolution of gas was limited not by the formation of nuclei, but by the growth of bubbles.

SURFACE-ACTIVE ADDITIONS AND CAVITATION

Additions of surface-active substances may exert a strong influence both on surface tension of metal and on the interphase energy at its interface with the hearth. This causes a change of the rim angle θ and affects the formation and growth of bubbles. In view of this the composition of metal assumes considerable importance, i.e, the presence in it of substances which powerfully reduce surface tension.

Problems pertaining to the wettability of refractory materials by molten ferrous metals were thoroughly studied by Levin /228/. He came to the conclusion that "the rim angle of a given alloy is greater with the material with which it is least apt to react and with which it produces a system closer to equilibrium."

Voluminous factual material relative to the liquid non-ferrous metal--fused salt systems is provided in the book by Belyayev and Zhemchuzhina /234/.

The influence of surface-active substances upon the intensification of heat exchange presents an interesting technological phenomenon.

Lozhkin and co-authors /236/, /237/ found that the coefficient of heat transfer from the walls to boiling mercury is small because of poor wettability and the formation of a vapor layer. To enhance gas evolution, they introduced small quantities of capillary active metals (potassium and sodium) into mercury. These additions reduced surface tension and clearing the contact surface of metal improved the wetting of the walls by mercury. As a result of this, the heat exchange coefficient increased tens of times.

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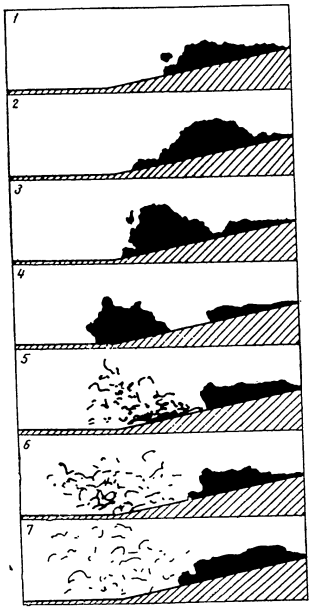

Fig. 255. Successive stages of the formation of cavitation bubble at the nozzle surface (diagram).

On the other hand, the introduction of oleic acid into aqueous solutions makes metal surfaces unwettable which leads to the "spreading" of bubbles along the heater and a changeover to "film" boiling characterized by low coefficient of heat exchange [238].

In conclusion, let us note still another possible source of gas phase nuclei formation. It is known that local stresses may develop as a result of rapid flow of liquid near solid bodies oscillating at high frequencies. If these stresses attain the ultimate strength of the liquid, then ruptures appear in it and the so-called cavitation bubbles arise [239].

Fig. 255 provides a diagram based on a cinematographic film showing the development of a cavitation bubble formed during the flow of water issued through a rectangular nozzle at a rate of 15-30 m/sec. It can be seen therefrom that this bubble originates at the narrowest section of the nozzle and moves without leaving the surface in the direction of the flow of water until it finally disappears.

Fig. 256 represents schematically the cavitation zone around a screw propeller. A spiral track can be distinguished here which is composed of bubbles carried away by the stream of liquid.

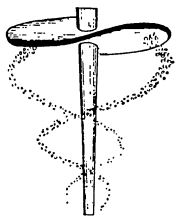

Fig. 256. Cavitation zone around a screw propeller (diagram).

It is still difficult to say what the significance of cavitation is for the process of decarbonization. One should think that, in spite of the powerful stirring of the open-hearth bath during boiling, it is hardly capable of giving rise to cavitation bubbles in appreciable quantities[1]. However, the possibility is not excluded that cavitation plays a certain role in the Bessemer process.

FORMATION OF BUBBLES AT THE METAL-SLAG INTERFACE AND FROTHING[2]

As mentioned previously, boiling during decarbonization may develop not only at the interface of metal with the hearth bed (bottom boil), but also at the contact surface with slag (surface boil). In the latter case the frothing of slag arises fairly often and this complicates very much the normal development of the melting process.

FORMATION OF BUBBLES

In the opinion of Andreyev [193] the appearance of bubbles at the metal-slag interface is facilitated by the fact that the work required for nuclei formation is considerably smaller here than in the volume of

1 It should, nevertheless, be expected that cavitation phenomena develop with greater effectiveness in supersaturated solutions than in unsaturated ones.

2 This section is written in collaboration with S. I. Popel'.

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metal. Apart from this, one should expect a greater supersaturation of steel in these regions (closeness to the oxidizing slag, lower total pressure, and so on). It is also enhanced by carbon and oxygen capillary activity which increases their concentrations at the contact surface [185], [218], [240].

Similar views are also held by other investigators. Thus, according to Sapiro [241] the variation of free energy during the formation of a bubble nucleus of critical size at the metal-slag interface may be expressed by equation

$$\Delta F = \frac{1}{3}(\sigma_{mg}\Delta S_{mg} + \sigma_{sg}\Delta S_{sg} - \sigma_{ms}\Delta S_{ms}) \cong$$

$$\cong \frac{1}{3}\sigma_{mg}\Delta S_{mg}\left(1 + \cos\theta_{sg} + \operatorname{ctg}^2\frac{\theta_{sg}}{2}\right). \qquad \text{(VIII, 366)}$$

Here σ_i and ΔS_i stand for corresponding interphase tensions and the increments of contact surfaces; θ_{s-g} is the rim angle as shown in fig. 257.

Since the surface tension of steel (σ_{m-g}) is ordinarily 2.5 - 3.5 times that of slag (σ_{s-g}), the interface area 1-3 noticeably exceeds that of 1-2 (see fig. 257). In other words, the emergence of a nucleus here is facilitated by the fact that the greater part of the surface requires less work during its formation.

Besides, the critical size of the bubble in this case must be approximately $\left(\frac{\sigma_{m-g}}{\sigma_{s-g}}\right) \cong 30$ times smaller than in the metal volume. Finally, the presence of solid unsintered slag particles at the boundary with metal also creates favorable conditions for the formation of bubbles.

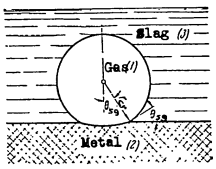

Fig. 257. Diagram of bubble at the slag-metal interface.

FROTHING

The frothing of slags is a highly undesirable phenomenon. It impairs the transfer of heat from the flame to the bath, retards the process, and leads to superheating of the furnace roof and ends.

Andreyev [193] distinguishes two types of slag froth - volume and surface. The first is formed in slags with increased viscosity where the rate of the emersion of bubbles is slower than the speed of their penetration into slag. Surface frothing is characteristic for fluid slags which possess, however, high surface viscosity. The latter hinders the running off of the film and prolongs the life of the bubbles.

In Sapiro's judgment [241], [242], [243], [244], frothing is facilitated by initial low surface tension of slag, its subsequent decrease due to adsorption of capillary-active substances, and the mechanical strength of the bubble film. He further believes that the envelope of the bubble consists of two parts -- the inside part formed during adsorption of substances dissolved in metal, and the external film formed at the slag-gas boundary. The higher is the viscosity of slag, the slower the run-off of the envelope and the more stable the bubble.

Sapiro states that two types of slag are subject to frothing -- either homogeneous ferrous slags or highly basic raw slags.

FACTORS DETERMINING THE STABILITY OF FROTH

Since the rate of bubble ingress into slag is determined by the process of decarbonization, then -- in order to prevent frothing -- it is necessary to reduce the period of gas presence in the slag layer. In particular, the rising speed of gas bubbles should be increased. It depends on the size of the bubbles, the viscosity of the medium, and other factors.

If the bubble was generated at the furnace bed, then it expands in rising both due to diminishing pressure and to absorption of gas from the bath. On the contrary, the bubbles formed at metal-slag interface are quite small and ascend slowly.

In view of the foregoing, surface boiling constitutes one of the factors which contribute to frothing. This is also facilitated by increased viscosity of slags. It reduces, for instance, the rising speed of the bubbles. Its significance was noted by Grum-Grzhimaylo [59], Schenk [61], and by other authors [243], [245].

Tests carried out with alcohol and water revealed [246] that adsorption of surface-active substances retards the movement of bubbles in solutions. A similar phenomenon is conceivable also in slags.

Alongside the viscosity of bubble motion, a substantial role is also played by the stability of its envelope. It is determined by a number of factors, the most important among which are - splitting pressure, sensitivity of adsorption to concentration changes, mechanical strength and surface separation.

Talmud and Bresler [247] with the aid of a movie camera (1 shot per 1/40 sec.) succeeded in establishing that in clear water a bubble explodes immediately on reaching the surface. Yet, if the bubble is protected by a layer of soap then it remains intact on the surface for a period up to 10 sec.

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Yerchikovsky [248] arrived at the conclusion that a rapid merging of bubbles coming from opposite directions takes place not only in pure liquids but also in certain diluted solutions (8.1% phenol and 0.9% KCl in H_2O).

Analogous results were obtained by Venstrem and Rebinder [249], as well as by other investigators [250].

Thus, a more or less stable foam is produced by solutions and not by pure liquids. The capillary-active substances which are to be found in the solutions, and which are responsible for the reduction of surface tension, increase the stability of froth.

SPLITTING PRESSURE

Deryagin and co-workers disclosed that solid surfaces pressed against each other separate after moistening by liquid.

Such splitting pressure manifests itself also when small particles covered by adsorption layers, as well as bubbles, approach each other. It comes into display usually at distances around 10^{-6} cm, attains a maximum at 10^{-7} to 10^{-8} cm, whereupon it begins to subside.

Tatiyevskaya [251], [252] succeeded in determining the splitting pressure developing when air bubbles draw together in water. In the presence of molecules of aliphatic acids, accumulated on the surface of the film, the latter becomes more stable. This is partly attributable to splitting pressure which prevents the bubbles from merging causing froth stability.

To the extent that slag and steel are not single component liquids but constitute solutions, adsorption phenomena should be expected to occur at their boundaries. As a matter of fact, experiments show [252] that a number of cations (Na^+, K^+, Ca^{2+}, etc.) and anions (PO_4^{3-}, $Si_xO_y^{z-}$ and so on) are capillary-active at the slag-gas interface. Their accumulation on the outer surface of the bubble envelope may prevent the bubbles from merging because of the electrostatic repulsion of the like ions.

Moreover, it is possible that splitting pressure also comes into display near the slag surface in impeding the bubbles to cross the boundary and thereby provoking frothing.

SENSITIVITY OF SURFACE TENSION TO THE CHANGE OF CONCENTRATION.

The bubble bursts in consequence of continuous diminishing of the envelope thickness. The latter is caused through imbibition of liquid into the sections with greater thickness (rims of the film), and also due to its run-off under the influence of the force of gravity [253]. With the film getting ever thinner, its surface increases while the concentration of capillary-active substances diminishes and becomes uneven. In consequence thereof, flows of liquid towards the thin spots of the

film develop in its surface layer. They are inverse to those which reduce the thickness of the film and this prolongs the life of the bubble.

Obviously, the greater the change of surface tension with concentration, the more intensive the inverse liquid flows are and the more stable the bubble becomes. An additional confirmation thereof is constituted by the fact that solutions of capillary-active substances froth most intensively when the surface layer is insufficiently saturated [254], i.e., in cases when the value of σ varies strongly with concentration.

A similar effect is to be expected to take place also in slags. Indeed, such substances like SiO_2 or P_2O_5 reduce appreciably the surface tension of ferrous oxide. In particular, the addition of 0.5% P_2O_5 causes σ to drop from 650 to 510 erg/cm^2, i.e., by 15%. In other words, adsorption may produce a considerable difference in surface tensions in the narrow and wide sections of the film and increase thereby the stability of the bubble.

MECHANICAL STRENGTH

Tests show that films which form the bubble envelope in aqueous solutions possess a definite viscosity, elasticity and shearing strength [255], [256], [257]. Moreover, soluble capillary-active substances produce adsorption layers the mechanical properties of which do not differ from those of a layer of pure water. The converse is apparent for hydrophilic colloids which have a smaller surface activity and form gel-like layers with high mechanical strength.

Thus according to Rebinder and Trapeznikov [255], the film on a 3% solution of saponin behaves as a two-dimensional solid body. Intrinsic to it are elastic properties and a mensurable tensile strength.

The mechanical properties of layers formed by substances insoluble in water vary depending on their nature.

In certain cases, they do not differ from the properties of a clear water layer, in other instances there appear films with considerable surface viscosity which produce plastic and even brittle fractures (see, e.g., [258], [259]).

This type of bubble stabilization is, no doubt, characteristic also for slag froth. Thus, Semik [260] revealed increased viscosity of the surface layer in blast furnace slags. He demonstrated that the critical shearing stress in slag at rest is greater than in slag with rapidly ruptured surface layer. In the latter case, the fracture lines of the film are discernible upon solidification. They have a different coloration than the rest of the slag surface.

The high mechanical strength and even the brittleness of slag froth may sometimes be registered during the melting process. It is apparently due to the increased contents of SiO_2 (or CaO) in the surface layer and

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to the presence of small particles of lime, magnesia, and other substances, wetted by slag.

SURFACE SEPARATION

Teitelbaum [261], [262], [263], in studying the solutions of organic liquids with similar surface tensions and viscosity, revealed a sharp maximum of froth stability for medium concentrations. In the absence of a common explanation for this fact, he advanced the theory of surface separation of such solutions.

It is assumed that the surface emulsoid which forms thereby increases sharply the viscosity of the film, stabilizing the froth.

On the basis of its existence, Teitelbaum explains the positive temperature coefficient of surface tension of the solutions which is to be registered at times (see page 307).

It should be noted however that Yerchikovsky [248] reached opposite conclusions. In his opinion, surface separation should reduce considerably the stability of froth.

Be that as it may, the possibility of surface emulsoid formation in liquid slags still seems to be quite conceivable.

The fact of the existence of volume separation speaks in favor of this theory. Volume separation, for example, in MeO - SiO_2 systems begins to develop at concentrations of silica which are the smaller the smaller is the radius of the Me^{2+} cation.

EFFECT OF INDIVIDUAL SLAG COMPONENTS

The available published communications on the influence of slag composition upon froth stability are often contradictory in character. Thus, Andreyev [193] believes that Al_2O_3 and CaF_2 prolong the life of a bubble. On the other hand, in slags containing CaO, FeO, and SiO_2 it is short.

Umrikhin [264] also observes that in heats run in basic open-hearth furnaces with slags containing a high percentage of Al_2O_3 the stability of froth and the period of its formation increase.

Revebtsov and Rybakov [265], on the contrary, came to the conclusion that in operations with aluminous slags no frothing is to be observed.

According to Sapiro [241], [243], [244] non-viscous slags with high contents of FeO and SiO_2 froth most frequently. In addition to this, the period of effervescent ore boil extends considerably at high concentrations of CaO + MgO ($\geq$ 50%) and low concentrations of Al_2O_3(2 - 4%). The addition of small portions of lime to acid slags reduces the duration of foaming.

As attested by certain data, [266], admixture of finely ground iron ore to a slag composition of 36% CaO, 22% SiO_2, 10% MnO and 11% FeO covering metal containing up to 6% C resulted in abundant evolution of gas not accompanied by frothing. Addition of Ca_2SiO_4, borax, and fluorite produced foaming which lasted for more than 10 min.

Finally observations show that addition of tar and mazut to gaseous fuel reduces the frothing of slag in open-hearth furnaces. Some authors [267] erroneously connect this with the increase of reducive properties of the gas jet, others [268] - with the growth of its caloricity. Sapiro [243] ascribes this effect to the mechanical destruction of the foam by the stream of the denser jet.

All the foregoing evidences that this problem is still insufficiently known and that further systematic investigation of the causes of slag frothing is required.

EMERSION OF BUBBLES

The emersion of bubbles concludes the process of decarbonization. At the same time it fulfills a number of very important functions.

First of all among them should be cited the development of the reaction front in the bath volume. The rising bubbles play the role of centers of gas evolution. They grow at the expense of the molecules of carbon monoxide they contain, as well as of the gases (N_2, H_2, etc.) dissolved in metal, and serve thus as active degasifiers of steel. Furthermore, the bubbles passing through slag react with iron oxides reducing them to metal or to ions of the lowest valence.

They produce an exceptionally important hydrodynamic influence on the bath by causing powerful mixing. This leads to a sharp increase of the coefficients of mass and heat transfer and also to the ejection of drops of metal into slag and into the atmosphere of the furnace. The latter fact produces a considerable effect on the saturation of steel with gases.

The efficiency of bath mixing may serve as a certain characteristic of these processes. As shown by Kocho [269] and Levin [270], the calculation of mixing efficiency made by Schenk is incorrect. It does not take into account the effect of the height on the work produced by the bubble. An assumption was made that the latter's volume is constant and that the work required for its passage into the gas phase is entirely absorbed by the bath.

Kocho improved the accuracy of this computation, having taken into consideration both the hydrostatic pressure and the expansion of the rising bubble. He also analyzed the case of the bubble's growth caused by the passage of CO molecules from the metal. At the same time, it was assumed that the volume of the bubble increases linearly with the height of its ascent.

Further elaboration for greater precision was accomplished by Levin,

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who took the site of bubble formation into account and based his calculations on a more correct regularity of the growth of bubble volumes while making an allowance for surface carbon oxidation.

The work of Pomerantsev and Syrkin [271] which deals with the ascent of bubbles presents a certain interest in that it provides a further detailization of the picture. They have established that a steady rate of ascent is being achieved here practically immediately.

Frank-Kamenetsky [272] succeeded in calculating the discoid shape of the rising bubble. Proceeding from the balance of the forces of surface tension and resistance to motion, he developed the following equation for velocity

$$v = \sqrt[4]{\frac{4g^3\sigma}{a^3(\gamma - \gamma')}}. \qquad \text{(VIII, 367)}$$

Here a = coefficient of resistance;
g = gravity acceleration;
γ_i = specific gravities.

In conclusion, let us dwell on the ejection of beads of metal by bubbles. Andreyev studied this phenomenon on a model by blowing air through mercury [193]. He found that the bubbles exploded immediately on a clear metal surface. This process decelerated, however, after the surface of mercury was covered with a layer of water. Moreover, upon the egress of the bubble from water, a rupture of the metallic film was to be observed together with the dispersion of mercury in the form of small drops. The replacement of water by transformer oil, producing a more stable foam, facilitated the passage through its layer of a greater number of bubbles.

Assuming that the quantity of metal carried away into the atmosphere of the furnace corresponds to 1/5 of the lifting power of bubbles, that only 1% of them actually reaches the gas-slag interface, and that the rate of carbon burn-out comprises 0.006% per minute, Andreyev determined that in a 100-ton capacity furnace around 500 kg of metal are being ejected into the gas phase per minute.

Medzhibozhsky investigated this process in industrial conditions. He reports that the number of metal beads contained in slag grows regularly with its diminishing viscosity and the increasing thickness of its layer (fig. 258) as well as with the rise of the carbon burn-out rate (fig. 259).

Further it became evident that the distribution of the beads along the height of the slag layer during intensive boiling is -- as one should have expected -- uneven. Their number is greater below (5.95%) and smaller at the top (0.81% at fluidity of 40 mm). Towards the end of ebulition this unevenness levels down.

It was established by chemical analysis that the contents of carbon in the beads of steel in slag is about half its contents in the

bath. Moreover, the concentration of C is lower in the bigger beads than in the smaller ones. This is probably due to the fact that the former originated from the bursting film, whereas the latter formed as a result of the ejection of drops of a more compact type.

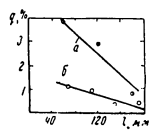

Fig. 258. Effect of slag fluidity (l, mm) and the thickness of slag layer (a - 135 mm, δ - 80 mm) on the contents of metal beads in slag (q, %)

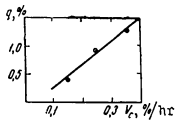

Fig. 259. Contents of metal beads in slag (q, %) vs. carbon burn-out rate.

On the basis of Stokes' formula and the conditions of steady process, Medzhibozhsky proposed a formula for the calculation of the number of beads ejected per second

$$q = \frac{3{,}81\, k P_{sl} r_k^2}{h_{sl}\eta_{sl}}, \qquad \text{(VIII, 368)}$$

where

q = rate of emergence of beads in relation to the weight of slag, % per minute;
k = their contents, %
P_{sl}, h_{sl}, & η = quantity in % to the weight of metal, thickness of the layer, and viscosity of slag;
r_k = mean radius of bead.

In particular, with $k = 0.5\%$, $h_{sl} = 8$ cm., $\eta_{sl} = 0.2 - 0.3$ poises, $r_k = 0.015$ cm., $P_{sl} = 8\%$, and $V_C = 0.2\%$ per hour, we have $q = 0.1\%$ per minute. The value produced is considerably smaller than that calculated by Andreyev.

Also of interest is the conclusion to the effect that the beads of metal introduce a relatively small quantity of oxygen into the bath, namely 0.005% per hour, while a far greater amount penetrates from slag - 0.48% per hour.

In summing up, one should emphasize once again the fact that the process of carbon burn-out is very complex and far too insufficiently studied. Its detailed and systematic investigation is essential.

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